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ALCOHOMETRIC TABLES, FOR EACH INTEGRAL PERCENTAGE BY WEIGHT, AND FOR EACH DEGREE OF THE HYDROGEN THERMOMETER FROM 15° TO 22°.

BY EDWARD W. MORLEY.

Received August 23, 1904.

THE following tables have been found so convenient in my laboratory that they are printed for the use of others. They give the true specific gravity for each integral percentage by weight from 0 per cent. to 100 per cent., for each degree of the centigrade hydrogen thermometer from 15° to 22°, according to the results of Mendeléeff. The temperature of 15°, prescribed in many tables, is suitable to warehouses where alcohol is gauged, but too low for scientific laboratories. The specific gravity here given is the quotient of the weight of the alcohol divided by its volume, increased by the correction for displaced air; in other words, it is the weight of 1 cc. of alcohol, the weight being reduced to vacuum.[1]

[1] Several methods of determining the specific gravity may be used. The following is convenient: Determine, first for all, the volume of a pycnometer at each degree from 15° to 22° (which requires but one weighing, but this must be corrected for displaced air and for the cubical expansion of the glass). The specific gravity is then found by dividing the weight of the alcohol, corrected for displaced air, by the capacity of the flask at the temperature of the alcohol. The following table gives the correction for displaced air, which is to be added for each gram of water or alcohol.

CORRECTION FOR DISPLACED AIR.

Specific gravity.	Correction for 1 gram. Gram.
0.80	+0.00109
0.85	+0.00108
0.90	+0.00107
0.95	+0.00106
1.00	+0.00106

Per cent.	$d\ \frac{15°}{4°}$.	$d\ \frac{16°}{4°}$.	$d\ \frac{17°}{4°}$.	$d\ \frac{18°}{4°}$.	Differences for 1 per cent.	Differences for 1°.
0	0.99913	0.99898	0.99881	0.99863	191	17
1	0.99724	0.99707	0.99690	0.99671	183	18
2	0.99542	0.99525	0.99506	0.99487	177	19
3	0.99366	0.99348	0.99329	0.99309	170	20
4	0.99197	0.99178	0.99159	0.99138	164	20
5	0.99034	0.99014	0.98994	0.98973	157	21
6	0.98878	0.98857	0.98837	0.98816	151	21
7	0.98728	0.98707	0.98686	0.98664	145	22
8	0.98583	0.98562	0.98541	0.98518	140	23
9	0.98444	0.98423	0.98400	0.98376	135	23
10	0.98310	0.98288	0.98265	0.98240	133	24
11	0.98180	0.98156	0.98131	0.98105	130	26
12	0.98053	0.98027	0.98000	0.97972	127	27
13	0.97929	0.97901	0.97872	0.97843	125	29
14	0.97806	0.97777	0.97747	0.97716	124	31
15	0.97685	0.97654	0.97622	0.97588	123	33
16	0.97565	0.97532	0.97498	0.97463	122	35
17	0.97446	0.97410	0.97375	0.97338	123	36
18	0.97326	0.97289	0.97251	0.97212	124	38
19	0.97204	0.97166	0.97127	0.97085	125	40
20	0.97082	0.97042	0.97001	0.96958	128	42
21	0.96957	0.96914	0.96871	0.96827	130	43
22	0.96830	0.96785	0.96740	0.96695	132	45
23	0.96700	0.96654	0.96608	0.96559	136	47
24	0.96567	0.96519	0.96471	0.96421	140	49
25	0.96431	0.96380	0.96330	0.96279	143	51
26	0.96291	0.96239	0.96186	0.96133	147	53
27	0.96147	0.96093	0.96038	0.95983	152	55
28	0.95997	0.95942	0.95886	0.95828	155	56
29	0.95845	0.95787	0.95729	0.95671	159	58
30	0.95688	0.95629	0.95569	0.95509	164	60

Per cent.	$d\ \frac{19°}{4°}$.	$d\ \frac{20°}{4°}$.	$d\ \frac{21°}{4°}$.	$d\ \frac{22°}{4°}$.	Differences for 1 per cent.	Differences for 1°.
0	0.99844	0.99824	0.99802	0.99780	194	21
1	0.99651	0.99630	0.99608	0.99585	186	22
2	0.99466	0.99445	0.99422	0.99399	180	22
3	0.99288	0.99265	0.99242	0.99218	172	23
4	0.99116	0.99093	0.99070	0.99045	166	23
5	0.98951	0.98927	0.98903	0.98878	159	24
6	0.98793	0.98768	0.98743	0.98718	153	25
7	0.98640	0.98615	0.98590	0.98564	148	25
8	0.98493	0.98468	0.98442	0.98415	143	26
9	0.98351	0.98326	0.98300	0.98271	137	26
10	0.98215	0.98189	0.98162	0.98133	140	27
11	0.98078	0.98049	0.98021	0.97991	137	28
12	0.97944	0.97913	0.97883	0.97852	133	30
13	0.97813	0.97781	0.97749	0.97716	133	32
14	0.97683	0.97649	0.97616	0.97581	131	34
15	0.97554	0.97519	0.97485	0.97448	130	35
16	0.97427	0.97390	0.97354	0.97316	129	37
17	0.97301	0.97262	0.97224	0.97185	130	38
18	0.97173	0.97134	0.97094	0.97052	131	40
19	0.97046	0.97003	0.96962	0.96919	132	42
20	0.96916	0.96872	0.96829	0.96784	135	44
21	0.96784	0.96738	0.96693	0.96645	137	46
22	0.96649	0.96601	0.96555	0.96506	140	47
23	0.96512	0.96462	0.96414	0.96364	143	49
24	0.96371	0.96320	0.96270	0.96218	146	51
25	0.96228	0.96175	0.96123	0.96068	150	53
26	0.96080	0.96025	0.95972	0.95916	155	54
27	0.95928	0.95872	0.95816	0.95759	159	56
28	0.95772	0.95713	0.95656	0.95596	163	58
29	0.95612	0.95552	0.95493	0.95432	166	60
30	0.95448	0.95387	0.95326	0.95263	169	62

Per cent.	$d\ \frac{15°}{4°}$.	$d\ \frac{16°}{4°}$.	$d\ \frac{17°}{4°}$.	$d\ \frac{18°}{4°}$.	Differences for 1 per cent.	Differences for 1°.
30	0.95688	0.95629	0.95569	0.95509	164	60
31	0.95527	0.95466	0.95405	0.95343	168	61
32	0.95361	0.95299	0.95236	0.95173	172	63
33	0.95191	0.95127	0.95063	0.94999	176	64
34	0.95018	0.94952	0.94886	0.94821	180	66
35	0.94840	0.94772	0.94705	0.94639	184	67
36	0.94658	0.94589	0.94522	0.94453	189	68
37	0.94472	0.94401	0.94332	0.94262	192	70
38	0.94282	0.94211	0.94140	0.94069	195	71
39	0.94089	0.04016	0.93944	0.93872	198	72
40	0.93893	0.93818	0.93746	0.93672	201	74
41	0.93694	0.93618	0.93544	0.93471	204	74
42	0.93491	0.93415	0.93340	0.93266	207	75
43	0.93284	0.93209	0.93134	0.93058	208	75
44	0.93078	0.93001	0.92925	0.92848	211	76
45	0.92868	0.92790	0.92714	0.92637	213	77
46	0.92655	0.92577	0.92501	0.92423	216	77
47	0.92440	0.92362	0.92285	0.92206	217	78
48	0.92224	0.92145	0.92068	0.91988	219	79
49	0.92006	0.91927	0.91849	0.91768	221	79
50	0.91786	0.91706	0.91627	0.91546	221	80
51	0.91565	0.91485	0.91405	0.91325	223	80
52	0.91343	0.91263	0.91182	0.91102	224	80
53	0.91119	0.91038	0.90957	0.90877	224	81
54	0.90895	0.90814	0.90733	0.90652	226	81
55	0.90669	0.90588	0.90506	0.90425	227	81
56	0.90442	0.90360	0.90279	0.90198	227	81
57	0.90215	0.90133	0.90052	0.89970	229	82
58	0 89987	0.89904	0.89822	0.89741	230	82
59	0.89757	0.89674	0.89593	0.89511	230	82
60	0.89527	0.89444	0.89362	0.89280	231	82

Per cent.	$d\ \frac{19°}{4°}$.	$d\ \frac{20°}{4°}$.	$d\ \frac{21°}{4°}$.	$d\ \frac{22°}{4°}$.	Differences for 1 per cent.	Differences for 1°.
30	0.95448	0.85387	0.95326	0.95263	169	62
31	0.95282	0.95219	0.95156	0.95093	173	63
32	0.95110	0.95047	0.94982	0.94918	177	64
33	0.94935	0.94870	0.94804	0.94738	180	65
34	0.94756	0.94691	0.94623	0.94556	185	66
35	0.94573	0.94506	0.94437	0.94369	189	68
36	0.94385	0.94316	0.94248	0.94178	194	69
37	0.94193	0.94123	0.94053	0.93983	196	70
38	0.93999	0.93927	0.93856	0.93785	200	71
39	0.93800	0.93728	0.93655	0.93582	203	73
40	0.93599	0.93525	0.93451	0.93377	203	74
41	0.93397	0.93323	0.93248	0.93173	206	75
42	0.93192	0.93117	0.93041	0.92966	209	75
43	0.92983	0.92908	0.92833	0.92756	212	76
44	0.92773	0.92696	0.92621	0.92544	214	76
45	0.92560	0.92483	0.92406	0.92329	216	77
46	0.92346	0.92268	0.92190	0.92113	219	78
47	0.92128	0.92050	0.91971	0.91992	220	79
48	0.91910	0.91830	0.91752	0.91672	222	79
49	0.91689	0.91609	0.91530	0.91449	223	80
50	0.91467	0.91386	0.91306	0.91225	222	80
51	0.91245	0.91164	0.91084	0.91002	223	81
52	0.91022	0.90941	0.90860	0.90779	225	81
53	0.90797	0.90715	0.90635	0.90553	226	81
54	0.90572	0.90490	0.90409	0.90327	227	81
55	0.90345	0.90263	0.90182	0.90099	228	82
56	0.90117	0.90035	0.89954	0.89871	229	82
57	0.89889	0.89807	0.89725	0.89642	230	82
58	0.89659	0.89577	0.89494	0.89412	231	82
59	0.89429	0.89346	0.89263	0.89181	231	83
60	0.89198	0.89115	0.89032	0.88949	232	83

Per cent.	$d\ \frac{15°}{4°}$.	$d\ \frac{16°}{4°}$.	$d\ \frac{17°}{4°}$.	$d\ \frac{18°}{4°}$.	Differences for 1 per cent.	Differences for 1°.
60	0.89527	0.89444	0.89362	0.89280	231	82
61	0.89296	0.89213	0.89131	0.89048	231	83
62	0.89065	0.88982	0.88899	0.88817	232	83
63	0.88833	0.88749	0.88667	0.88584	233	83
64	0.88600	0.88516	0.88433	0.88350	233	83
65	0.88367	0.88283	0.88200	0.88116	234	84
66	0.88133	0.88049	0.87966	0.87882	235	84
67	0.87898	0.87814	0.87730	0.87646	235	84
68	0.87663	0.87578	0.87495	0.87411	236	84
69	0.87428	0.87343	0.87259	0.87175	237	84
70	0.87191	0.87106	0.87022	0.86938	238	84
71	0.86954	0.86869	0.86785	0.86700	239	85
72	0.86715	0.86630	0.86546	0.86461	239	85
73	0.86476	0.86391	0.86306	0.86221	239	85
74	0.86237	0.86152	0.86067	0.85982	242	85
75	0.85996	0.85910	0.85825	0.85740	242	85
76	0.85754	0.85669	0.85584	0.85497	242	85
77	0.85513	0.85427	0.85342	0.85256	243	86
78	0.85270	0.85184	0.85099	0.85012	245	86
79	0.85025	0.84939	0.84853	0.84767	245	86
80	0.84780	0.84694	0.84608	0.84521	246	86
81	0.84534	0.84448	0.84362	0.84274	248	87
82	0.84286	0.84189	0.84113	0.84026	249	87
83	0.84037	0.83950	0.83864	0.83776	251	87
84	0.83786	0.83699	0.83613	0.83525	253	87
85	0.83533	0.83446	0.83359	0.83271	255	87
86	0.83278	0.83191	0.83104	0.83016	258	87
87	0.83021	0.82934	0.82846	0.82758	261	87
88	0.82760	0.82673	0.82586	0.82498	263	87
89	0.82498	0.82411	0.82323	0.82235	265	87
90	0.82233	0.82146	0.82058	0.81970	268	87

Per cent.	$d\ \frac{19°}{4°}$	$d\ \frac{20°}{4°}$	$d\ \frac{21°}{4°}$	$d\ \frac{22°}{4°}$	Differences for 1 per cent.	Differences for 1°.
60	0.89198	0.89115	0.89032	0.88949	232	83
61	0.88966	0.88883	0.88800	0.88717	232	83
62	0.88734	0.88651	0.88568	0.88485	233	83
63	0.88501	0.88418	0.88334	0.88251	234	83
64	0.88267	0.88184	0.88100	0.88017	234	83
65	0.88033	0.87950	0.87866	0.87783	235	83
66	0.87799	0.87715	0.87631	0.87548	236	84
67	0.87563	0.87479	0.87395	0.87312	236	84
68	0.87327	0.87243	0.87159	0.87074	236	84
69	0.87092	0.87007	0.86923	0.86838	238	84
70	0.86854	0.86769	0.86685	0.86600	238	85
71	0.86616	0.86531	0.86447	0.86362	240	85
72	0.86376	0.86291	0.86206	0.86122	240	85
73	0.86137	0.86051	0.85966	0.85881	240	85
74	0.85897	0.85811	0.85726	0.85621	242	85
75	0.85655	0.85569	0.85483	0.85398	242	86
76	0.85413	0.85327	0.85241	0.85155	243	86
77	0.85171	0.85084	0.84998	0.84912	244	86
78	0.84927	0.84840	0.84754	0.84667	246	86
79	0.84681	0.84594	0.84507	0.84421	246	87
80	0.84435	0.84348	0.84261	0.84173	247	87
81	0.84188	0.84101	0.84014	0.83926	249	87
82	0.83940	0.83852	0.83765	0.83677	250	87
83	0.83690	0.83603	0.83515	0.83427	252	87
84	0.83439	0.83351	0.83263	0.83175	254	88
85	0.83185	0.83097	0.83009	0.82920	256	88
86	0.82929	0.82841	0.82754	0.82664	258	88
87	0.82672	0.82583	0.82496	0.82406	261	88
88	0.82411	0.82323	0.82235	0.82145	263	88
89	0.82149	0.82060	0.81972	0.81882	266	88
90	0.81883	0.81794	0.81706	0.81616	267	88

Per cent.	$d\ \frac{15°}{4°}$.	$d\ \frac{16°}{4°}$.	$d\ \frac{17°}{4°}$.	$d\ \frac{18°}{4°}$.	Differences for 1 per cent	Differences for 1°.
90	0.82233	0.82146	0.82058	0.81970	268	87
91	0.81965	0.81878	0.81791	0.81703	271	87
92	0.81694	0.81607	0.81520	0.81432	276	87
93	0.81418	0.81331	0.81244	0.81157	280	87
94	0.81138	0.81051	0.80965	0.80878	283	87
95	0.80854	0.80768	0.80682	0.80595	289	86
96	0.80565	0.80479	0.80394	0.80306	294	86
97	0.80271	0.80185	0.80100	0.80013	298	86
98	0.79972	0.79887	0.79802	0.79715	304	85
99	0.79668	0.79583	0.79498	0.79412	310	85
100	0.79357	0.79272	0.79188	0.79102	...	85

Squibb made careful and elaborate studies of the specific gravity of absolute alcohol and of mixtures of alcohol and water. It was important to learn whether his skill as a manufacturer had produced an alcohol of lower specific gravity than that of Mendeléeff. First, I applied to Squibb's published results the correction for displaced air; then I selected all his values for alcohol of more than 90 per cent., computed the corresponding values according to Mendeléeff, found the difference of each pair of values and took the mean of these differences. If we consider all the 25 differences, Squibb's absolute alcohol appears lighter than that of Mendeléeff by 0.00005; if we select the 15 experiments of Squibb in which temperature errors were likely to be less, his alcohol appears heavier than that of Mendeléeff by 0.00003. Both these figures cannot be distinguished from Squibb's errors of observation, and afford ground for believing that Mendeléeff's absolute alcohol has not been surpassed. It may also be said that the scale of Squibb's thermometer is not sufficiently defined in the record, and that his reading of temperatures was not close.

These tables accordingly depend on Mendeléeff; they have been recomputed to the scale of the hydrogen thermometer, to which fine thermometers are now commonly adjusted. Interpolations have been made with care, by two different formulae where

Per cent.	$d\ \frac{19°}{4°}$.	$d\ \frac{20°}{4°}$.	$d\ \frac{21°}{4°}$.	$d\ \frac{22°}{4°}$.	Differences for 1 per cent.	Differences for 1°.
90	0.81883	0.81794	0.81706	0.81616	267	88
91	0.81616	0.81527	0.81440	0.81350	270	88
92	0.81345	0.81257	0.81170	0.81081	274	88
93	0.81071	0.80982	0.80895	0.80807	278	88
94	0.80792	0.80704	0.80617	0.80529	282	87
95	0.80509	0.80421	0.80335	0.80249	287	87
96	0.80221	0.80134	0.80049	0.79962	293	86
97	0.79928	0.79841	0.79756	0.79670	297	86
98	0.79631	0.79544	0.79458	0.79373	302	86
99	0.79328	0.79241	0.79156	0.79072	309	85
100	0.79018	0.78932	0.78847	0.78763		85

possible. But from 5 per cent. to 15 per cent., interpolation for expansion is uncertain at the higher temperatures, in some cases by as much as 0.0010. The same is true, in a less degree, near 40 per cent. For mixtures of these percentages, where special accuracy is required, observations may be made below 18°.

[Contribution from the Department of Food and Drug Inspection of the Massachusetts State Board of Health.]

A COMPARATIVE REFRACTOMETER SCALE FOR USE WITH FATS AND OILS.

By Albert E. Leach and Hermann C. Lythgoe.

Received July 27, 1904.

The indices of refraction of substances vary with the temperature, the refraction becoming less as the temperature is raised. It has been shown by the work of Olds, Long, Proctor, and Tolman that this variation is a constant for certain oils and fats (notably the edible oil and fats) and its value is 0.000365 for each degree centigrade. This relation has been substantiated by the writers.

Recently the Zeiss butyro-refractometer has come into use to a large extent for the examination of oils and fats, partly on account of its cheapness in comparison with other instruments for the same purpose, but principally on account of its ease of manipu-

lation, and from the fact that its scale is within the range of the refractions of the fixed oils and fats.

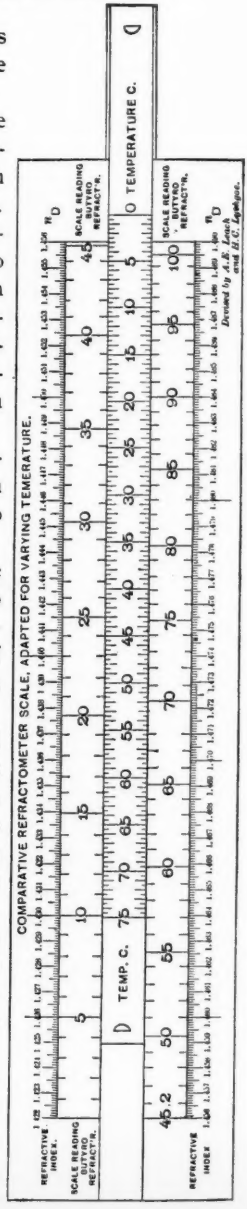
This instrument has an arbitrary scale from 0 to 100, covering the indices of refraction from 1.4220 to 1.4895, which scale is not uniform with the values of n_D. Thus the differences from 0 to 10 in indices of refraction is 0.0080 and from 90 to 100 is 0.0055; consequently the variation with the temperature of oils on the arbitrary scale of the instrument is not constant except for slight changes of temperature, and this variation changes with different parts of the scale.

Thus the variation for 1° C. on the refractometer is 0.46 for readings between 0 to 10, and 0.66 for readings between 90 and 100.

The best methods of obtaining scale readings at different temperatures is to first transform them into values of n_D, apply the correction, getting the values of n_D at the required temperatures, then transform into scale readings.

In order to do away with this extended calculation the writers have devised the slide-rule illustrated. The values of n_D are constant, and the values of the butyro scale have been laid off against the index of refraction scale, according to the table of Pulfrich, published by Zeiss and Jena. The sliding temperature scale (from 0 to 75° C.) has a value of 0.027375 on the index of refraction scale, making each degree centigrade equal to 0.000365 on the scale of indices of refraction.

By the use of this slide-rule, readings may be obtained on the scale of the butyro-refractometer at different temperatures,


COMPARATIVE REFRACTOMETER SCALE, ADAPTED FOR VARYING TEMERATURE.
TEMPERATURE C.
TEMP. C.
SCALE READING BUTYRO REFRACT'R.
REFRACTIVE INDEX.
Devised by A.E. Leach and H.C. Lythgoe.

without first transforming them into indices of refraction, readings in indices of refraction may be obtained at different temperatures without calculation, and readings on either refractometer scale may be readily transformed into readings on the other.

In using this rule the slide is moved until the initial temperature and refraction coincide, then opposite the required temperature is found the corresponding refraction. If this temperature falls outside of the refraction scale it will be necessary to shift the slide, for example:

At 35.5° C. an oil reads 40.1 on the butyro-refractometer. Required, its refraction at 20°. Place the slide so that 35.5 on the slide coincides with 40.1 on the butyro scale, then it will be seen that the right end of the refractometer scale (45.2) exactly coincides with 25° on the slide. Move the slide until 25 coincides with 45.2 on the lower scale, then opposite 20 on the slide read 47.7.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

THE DETECTION OF WATERED MILK.

BY ALBERT E. LEACH AND HERMANN C. LYTHGOE.

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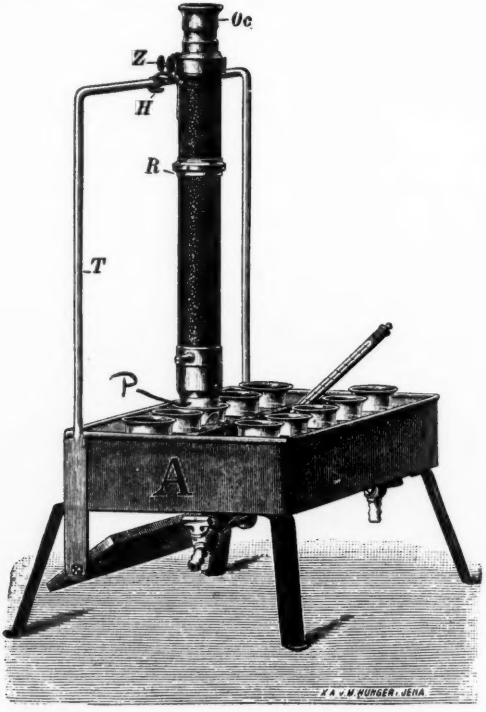
ONE of the most difficult problems with which the analyst is confronted is that of distinguishing between what might be termed honest low-standard milk, or milk below the standard coming from the cow as such, and milk that is fraudulently watered. Judgment on this point has heretofore been based largely on the relative proportion of fat to solids not fat, taken in connection with an abnormally low percentage of total solids. Additional information on this question is furnished by the density of the milk serum when the milk has been curdled under fixed conditions, though this in itself is by no means conclusive.

The addition of water to milk perceptibly affects the degree of refraction of the serum to such an extent that this latter constant promises to be a most helpful one in determining whether or not the milk has been watered. For this purpose the immersion refractometer of Zeiss is most useful, although the Abbé refractometer may be employed.

The Zeiss Immersion Refractometer.—The construction of this instrument is such that, as its name implies, it may be directly immersed in a solution, the degree of refraction of which, within limits, may be determined upon an arbitrary scale. The accompanying figure shows this instrument.



P is a glass prism, fixed in the lower end of the tube of the instrument, while at the top of the tube is the ocular *Oc*, and just below this on a level with the vernier screw *Z* is the scale, on which is read the degree of refraction of the liquid in which the prism *P* is immersed. The tube may be held in the hand and directly dipped in the liquid to be tested, this liquid being contained in a vessel with a transparent bottom, through which the light is reflected. The preferable method of use is, however, that shown in the figure.

A is a metal bath with inlet and outlet tubes, arranged whereby water is kept at a constant level. The water is maintained at a constant temperature by means of a controller or refractometer heater. In the bath *A* are immersed a number of beakers, containing the solutions to be tested. *T* is a frame on which is hung the refractometer by means of the hook *H*, at just the right height to permit of the immersion of the prism *P* in the liquid in any of the beakers in the row beneath. Under this row of beakers the bottom of the tank is composed of a strip of ground glass, through which light is reflected by an adjustable, pivoted mirror.

The temperature of the bath is noted by a delicate thermometer immersed therein, capable of reading to tenths of a degree.

Returning to the main refractometer-tube, *R* is a graduated ring or collar, which is connected by a sleeve within the tube with a compound prism near the bottom, the construction being such that by turning the collar *R* one way or the other the chromatic aberration or dispersion of any liquid may be compensated for, and a clear-cut shadow or critical line projected across the scale. By the graduation on the collar *R* the degree of dispersion may be read. Tenths of a degree on the main scale of the instrument may be read with great accuracy by means of the vernier screw *Z*, graduated along its circumference, the screw being turned in each case till the critical line on the scale coincides with the nearest whole number.

If the immersion refractometer is unavailable, and the analyst is provided with the Abbé instrument, indices of refraction as read on the Abbé may be converted into scale readings of the immersion refractometer by the following table:

n_D.	Scale reading.	n_D.	Scale reading.	n_D.	Scale reading.	n_D.	Scale reading.
1.3390	30.0	1.3410	35.3	1.3430	40.6	1.3450	45.9
1.3391	30.3	1.3411	35.6	1.3431	40.8	1.3451	45.2
1.3392	30.6	1.3412	35.8	1.3432	41.1	1.3452	45.5
1.3393	30.8	1.3413	36.1	1.3433	41.4	1.3453	45.7
1.3394	31.1	1.3414	36.3	1.3434	41.6	1.3454	47.0
1.3395	31.3	1.3415	36.6	1.3435	41.9	1.3455	47.3
1.3396	31.6	1.3416	36.9	1.3436	42.2	1.3456	47.5
1.3397	31.9	1.3417	37.1	1.3437	42.4	1.3457	47.8
1.3398	32.1	1.3418	37.4	1.3438	42.7	1.3458	48.0
1.3399	32.4	1.3419	37.7	1.3439	43.0	1.3459	48.3
1.3400	32.7	1.3420	37.9	1.3440	43.2	1.3460	48.6
1.3401	32.9	1.3421	38.2	1.3441	43.5	1.3461	48.9

n_D.	Scale reading.	n_D.	Scale reading.	n_D.	Scale reading.	n_D.	Scale reading.
1.3402	33.2	1.3422	38.5	1.3442	43.8	1.3462	49.1
1.3403	33.4	1.3423	38.7	1.3443	44.0	1.3463	49.4
1.3404	33.7	1.3424	39.0	1.3444	44.3	1.3464	49.7
1.3405	34.0	1.3425	39.3	1.3445	44.6	1.3465	49.9
1.3406	34.2	1.3426	39.5	1.3446	44.8	1.3466	50.2
1.3407	34.5	1.3427	39.8	1.3447	45.1	1.3467	50.5
1.3408	34.8	1.3428	40.0	1.3448	45.4	1.3468	50.7
1.3409	35.0	1.3429	40.3	1.3449	45.6	1.3469	51.0

Method of Procedure.—The method of curdling milk, employed in this laboratory, is that of Woodman[1]—as follows:

To 100 cc. of milk, at a temperature of about 20° C., are added 2 cc. of 25 per cent. acetic acid (sp. gr. 1.0350) in a beaker, and the beaker, covered with a watch-glass, is heated in a water-bath for twenty minutes at a temperature of 70° C. After this the beaker is placed in ice-water for ten minutes, and the solution filtered. The refractometer is placed directly in the clear filtrate. Table I shows analyses of milk selected from a wide range of samples regularly collected and examined in the routine of inspection.

TABLE I.—CONSTANTS OF MILK AND MILK SERUM. LABORATORY SAMPLES.

Determinations on milk.						On milk serum.	
Total solids. Per cent.	Water. Per cent.	Fat. Per cent.	Solids, not fat. Per cent.	Ash. Per cent.	Spec. grav. at 15° C.	Spec. grav. at 15° C.	Immersion refractometer reading at 20° C.
16.45	83.55	8.20	8.25	...	1.0255	1.0274	40.95
15.90	84.10	7.00	8.90	0.69	1.0277	1.0285	42.00
14.37	85.63	5.50	8.88	0.58	1.0282	1.0280	42.40
14.17	85.83	4.85	9.32	0.62	1.0313	1.0281	44.20
14.04	85.96	4.95	9.09	0.60	1.0303	1.0274	42.70
13.80	86.20	5.00	8.80	0.65	1.0302	1.0289	42.75
13.59	86.41	4.30	9.29	0.64	1.0321	1.0285	44.50
13.39	86.61	4.40	8.99	0.50	1.0324	1.0285	43.70
13.28	86.72	4.40	8.88	0.60	1.0299	1.0289	42.65
13.12	86.88	4.00	9.12	0.59	1.0317	1.0280	43.75
13.00	87.00	4.30	8.70	0.56	1.0310	1.0266	42.60
12.90	87.10	3.85	9.05	0.61	1.0318	1.0289	43.40
12.80	87.20	4.30	8.50	0.46	1.0304	1.0277	42.70
12.70	87.30	3.80	8.90	0.53	1.0314	1.0280	43.10
12.63	87.37	3.50	9.13	0.65	1.0323	1.0277	43.65
12.62	87.38	4.10	8.52	0.52	1.0298	1.0272	42.40

[1] This Journal, **21**, 503 (1899).

Determinations on milk.						On milk serum.	
Total solids. Per cent.	Water. Per cent.	Fat. Per cent.	Solids, not fat. Per cent.	Ash. Per cent.	Spec. grav. at 15° C.	Spec. grav. at 15° C.	Immersion refractometer reading at 20° C.
12.57	87.43	3.70	8.87	0.68	1.0317	1.0278	43.45
12.47	87.53	3.60	8.87	0.65	1.0303	1.0282	43.15
12.36	87.64	3.20	9.16	0.55	1.0327	1.0282	43.25
12.30	87.70	3.20	9.10	0.62	1.0327	1.0283	44.00
12.16	87.84	4.35	7.81	0.49	1.0275	1.0265	41.10
12.00	88.00	3.40	8.60	0.62	1.0275	1.0280	41.75
11.86	88.14	3.60	8.26	0.49	1.0306	1.0266	42.40
11.67	88.33	3.95	7.77	0.48	1.0265	1.0240	39.30
11.60	88.40	2.75	8.85	0.65	1.0320	1.0282	43.55
11.50	88.50	3.45	8.05	0.51	1.0290	1.0269	41.40
11.40	88.60	3.10	8.30	0.60	1.0297	1.0278	42.00
11.25	88.75	2.80	8.45	0.58	1.0282	1.0274	40.90
11.07	88.93	3.00	8.07	0.62	1.0290	1.0270	40.75
10.69	89.31	2.95	7.74	...	1.0288	1.0262	39.85
10.25	89.75	3.20	6.95	0.55	1.0230	1.0223	36.40
8.34	91.66	2.20	6.14	0.38	1.0224	1.0207	34.70

Table II shows analyses of a whole milk submitted to varying degrees of watering up to 50 per cent. of added water.

TABLE II.—CONSTANTS OF MILK AND MILK SERUM. A WHOLE MILK SYSTEMATICALLY WATERED.

	Determinations on milk.						On milk serum.	
Water added. Per cent.	Total solids. Per cent.	Water. Per cent.	Fat. Per cent.	Solids, not fat. Per cent.	Ash. Per cent.	Spec. grav. at 15° C.	Spec. grav. at 15° C.	Immersion refractometer reading at 20° C.
0	12.65	87.35	4.00	8.65	0.65	1.0315	1.0287	42.40
10	11.33	88.67	3.50	7.83	0.60	1.0278	1.0260	39.75
20	10.10	89.90	3.10	7.00	0.53	1.0252	1.0230	36.90
30	8.95	91.05	2.80	6.15	0.48	1.0211	1.0200	34.10
40	7.67	92.33	2.40	5.27	0.40	1.0192	1.0167	31.10
50	6.43	93.57	2.00	4.43	0.38	1.0154	1.0140	28.45

Table III shows a centrifugally skimmed milk, systematically watered up to 50 per cent. of added water as in Table II. It will be observed that both the specific gravity and immersion refractometer readings of the serum in Table II agree very closely with those of the skimmed milk in Table III, having a corresponding amount of water.

TABLE III.—CONSTANTS OF MILK AND MILK SERUM. A SKIMMED MILK SYSTEMATICALLY WATERED.

	Determinations on milk.						On milk serum.	
Water added. Per cent.	Total solids. Per cent.	Water. Per cent.	Fat. Per cent.	Solids, not fat. Per cent.	Ash. Per cent.	Spec. grav. at 15° C.	Spec. grav. at 15° C.	Immersion refractometer reading at 20° C.
0	9.05	90.95	0.03	9.02	0.64	1.0350	1.0296	42.85
10	8.14	91.85	0.03	8.11	0.60	1.0317	1.0260	39.60
20	7.27	92.73	0.02	7.25	0.56	1.0278	1.0230	36.85
30	6.41	93.59	0.02	6.39	0.48	1.0247	1.0200	34.00
40	5.50	94.50	0.01	5.49	0.44	1.0209	1.0170	31.20
50	4.61	95.39	0.01	4.60	0.39	1.0172	1.0140	28.50

A comparison of the immersion refractometer readings of the sera of milk of varied quality shows at once that the refraction of the serum is a general index to watering. A reading below 40°, with the above conditions carefully observed, seems to indicate added water.

Table IV shows results of analyses of milk of known purity, taken from an exceptionally well-fed herd of Holstein cows,[1] milked in the presence of one of the inspectors. The daily rations of each cow consisted of 6 quarts of shorts, 2 quarts of cottonseed meal and 2 quarts of corn-meal with hay.

As showing what similar conditions prevail between fancy-bred stock, as shown above, and the more common Holsteins, kept under ordinary farm conditions, Table V gives data of the milk of a herd of the latter variety, this milk being taken in the presence of one of the writers. The daily rations in this case consisted of 3 quarts of meal, 2 quarts of mixed feed, 2 quarts of gluten, with green fodder.

In no case has there yet been found a refractometer reading of less than 39 at 20° C. for the serum of pure milk. With our present knowledge, 39 would seem to be a reasonable minimum figure, below which a sample could be declared fraudulently watered when the conditions of the test are carried out precisely as above described.

The following table is convenient for calculation of the reading to 20° C. when it is difficult to keep the water-bath at exactly 20°:

[1] This is a prize herd, carefully bred for exhibition purposes. In spite of this, the very low average quality of the milk should be noted.

TABLE IV.—MILK OF KNOWN PURITY FROM FANCY HOLSTEIN COWS.

		Determinations on milk.								On milk serum.		
Age of cow. Years.	Time since calving. Months.	Specific gravity at 15° C.	Water. Per cent.	Total solids. Per cent.	Fat. Per cent.	Solids not fat. Per ct.	Ash. Per cent.	Milk-sugar. Per ct.	Proteids. Per cent.	Specific gravity at 15° C.	Immersion refractometer reading at 20° C.	n_D. 20°.
2	2	1.0317	87.26	12.74	3.70	9.04	0.60	4.80	3.64	1.0297	44.4	1.344408
3	4	1.0303	87.37	12.63	4.00	8.36	0.66	4.55	3.42	1.0290	42.8	1.343804
6	12	1.0296	87.68	12.32	3.90	8.42	0.63	4.20	3.59	1.0286	42.3	1.343614
3	4	1.0307	87.77	12.23	3.80	8.43	0.50	4.20	3.73	1.0289	42.9	1.343842
6	12	1.0296	87.84	13.16	3.45	8.71	0.60	4.10	4.01	1.0297	43.5	1.344070
2	2	1.0312	87.88	12.12	3.40	8.72	0.74	4.75	3.23	1.0329	44.5	1.344445
7	12	1.0301	88.11	11.89	3.40	8.49	0.70	4.35	3.44	.....	43.7	1.344146
12	5	1.0301	88.24	11.76	3.40	8.36	0.54	4.80	3.02	.....	42.9	1.343842
2	2	1.0289	88.33	11.67	3.55	8.12	0.60	4.50	3.02	1.0297	43.2	1.343956
5	4	1.0300	88.37	11.63	3.30	8.33	0.58	4.75	3.00	1.0289	43.6	1.344108
4	6	1.0297	88.41	11.59	3.20	8.39	0.62	4.40	3.31	1.0290	42.9	1.343842
5	½	1.0304	88.43	11.57	3.30	8.27	0.62	4.70	2.95	1.0318	43.0	1.343880
3	4	1.0311	88.51	11.49	3.25	8.24	0.62	4.35	3.27	1.0293	44.1	1.344297
6	1	1.0291	88.52	11.48	3.35	8.13	0.67	4.70	2.76	1.0290	42.8	1.343804
2	2	1.0296	88.53	11.47	3.45	8.02	0.55	4.60	2.87	1.0288	43.1	1.343918
2	2	1.0298	88.70	11.30	3.30	8.00	0.64	4.70	2.66	1.0277	42.1	1.343538
5	7	1.0283	88.82	11.18	3.20	7.98	0.60	3.95	3.43	1.0260	40.5	1.342940
2	2	1.0292	88.84	11.16	3.00	8.16	0.61	4.30	3.25	1.0285	41.6	1.343352
2	2	1.0292	88.93	11.07	2.95	8.12	0.55	4.60	3.02	.....	42.1	1.343538
2	2	1.0290	89.26	10.74	2.95	7.79	0.74	4 25	2.80	1.0280	40.6	1.342978
4	5	1.0262	89.29	10.71	3.25	7.46	0.55	4.00	2.91	1.0279	40.0	1.342750
2	1½	1.0293	89.41	10.59	2.55	8.04	0.52	4.30	3.22	1.0290	41.8	1.343426
	Highest,	1.0371	89.41	12.74	4.00	9.04	0.74	4.80	4.01	1.0329	44.4	1.344408
	Lowest,	1.0262	87.26	10.59	2.55	7.46	0.50	3.95	2 76	1.0260	40.0	1.342750
	Average,	1.0297	88.39	11.61	3.34	8.27	0.61	4.45	3.21	1.0291	42.7	1.343766

TABLE V.—MILK OF KNOWN PURITY FROM COMMON HOLSTEIN COWS.

Age of cow. Years.	Time since calving. Months.	Determinations on milk. Specific gravity at 15° C.	Water. Per cent.	Total solids. Per cent.	Fat. Per cent.	Solids not fat. Per ct.	Ash. Per cent.	Milk-sugar. Per ct.	Proteids. Per cent.	On milk serum. Specific gravity at 15° C.	Immersion refractometer reading at 20° C.	$n_{D.}$ 20°.
6	1	1.0290	87.24	12.76	4.50	8.26	0.52	4.90	2.84	1.0253	42.9	1.343842
5	2	1.0297	87.32	12.68	4.10	8.58	0.45	4.90	3.23	1.0295	43.1	1.343918
3	9	1.0305	87.87	12.13	3.55	8.58	0.55	4.35	3.68	1.0287	41.5	1.343315
8	3	1.0302	87.89	12.11	3.65	8.46	0.50	4.90	3.06	1.0291	42.0	1.343500
5	3	1.0296	88.07	11.93	3.45	8.48	0.60	4.30	3.58	1.0271	41.4	1.343278
7	1½	1.0307	88.24	11.76	3.60	8.16	0.50	4.80	2.86	1.0291	42.1	1.343538
2	3	1.0295	88.32	11 68	3.30	8.38	0.49	4.65	3.24	1.0285	41.8	1.343426
6	4	1.0300	88.60	11.40	3.05	8.35	0.60	4.55	3.20	1.0287	40.9	1.343092
5	8	1.0285	88.83	11.17	3.25	7.92	0.53	4.10	3.29	1.0286	39.7	1.342636
6	9	1.0290	88.90	11.10	3.30	7.80	0.65	3.95	3.25	1.0266	39.9	1.342712
7	7	1.0286	89.44	10.56	2.70	7.86	0.63	3.75	3.48	1.0296	39.0	1.342370
2	2	1.0286	89.55	10.45	2.60	7.45	0.59	4.25	3.01	1.0267	40.0	1.342750
	Highest,	1.0307	89.55	12.76	4.50	8.58	0.60	4.90	3.68	1.0296	43.1	1.343918
	Lowest,	1.0282	87.24	10.45	2.60	7.80	0.45	3.75	2.84	1.0253	39.0	1.342370
	Average,	1.0295	88.35	11.65	3.45	8.22	0.54	4.45	3.23	1.0281	41.6	1.34352

TABLE VI.—READINGS OF MILK SERUM ON THE IMMERSION REFRACTOMETER REDUCED TO 20°.

Temp.	Scale readings. 36.	37.	38.	39.	40.	41.	42.	43.	44.	45.
15°	34.75	35.75	36.75	37.75	38.75	39.75	40.70	41.70	42.65	43.65
16	35.05	36.05	37.05	38.05	39.05	40.05	41.00	41.95	42.90	43.85
17	35.25	36.25	37.25	38.25	39.25	40.25	41.20	42.20	43.15	44.10
18	35.50	36.50	37.50	38.50	39.50	40.50	41.45	42.45	43.40	44.40
19	35.75	36.75	37.75	38.75	39.75	40.75	41.75	42.75	43.70	44.70
20	36.00	37.00	38.00	39.00	40.00	41.00	42.00	43.00	44.00	45.00
21	36.25	37.25	38.25	39.30	40.30	41.30	42.30	43.30	44.30	45.30
22	36.50	37.50	38.50	39.55	40.60	41.60	42.60	43 60	44.60	45.60
23	36.80	37.80	38.80	39.85	40.90	41.90	42.90	43.90	44.90	45.90
24	37.10	38.10	39.10	40.15	41.20	42.20	43.20	44.20	45.20	46.20
25	37.40	38.40	39.40	40.45	41.50	42.50	43.50	44.50	45.40	46.50

Example.—If at 25° the milk serum reads 42.3, the correct reading at 20° is 43.5 + 0.3 = 43.8.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

COMPOSITION AND ADULTERATION OF GROUND MUSTARD.

BY ALBERT E. LEACH.

Received July 27, 1904.

MUSTARD has long taken the lead as the most extensively adulterated of all the spices, especially in localities where no system of food inspection prevails. The custom of deliberately mixing cereal flour or starch with ground mustard was practiced for many years, and, in fact, continued long after the serious adulteration of other spices had been held in check by the increased enforcement of pure food laws.

Coloring with turmeric was also a time-honored custom, and, in fact, still prevails, except in localities where the public have been educated to view with suspicion the deep yellow color of the product. Of late the employment of other colors than turmeric, such, for example, as various of the oil-soluble coal-tar dyes, has arisen to claim the attention of the analyst.

All the above forms of gross sophistication can, without doubt, be dealt with by almost any food commission or health board having in charge the enforcement of pure food laws, acting under the general food laws of their state, and without the fixing of definite standards. It is, however, in connection with other and perhaps milder forms of adulteration of mustard that the necessity of carefully fixed standards are of greater importance. The questions of how much starch, if any, should be allowed in ground mustard, due to weed seeds, and whether mustard hulls have been mixed with the mustard "flour" in excess of the amount found in the whole seed, should be largely settled by appropriate standards, if possible.

Commercial mustard "flour," unlike the other spices, is not ground from the whole seed, but is a manufactured product, being deprived, as a rule, of a large portion of the fixed oil and most of the hulls, so as to insure a fine, even powder. Hence in fixing standards for what the trade understands as mustard flour, difficulties are met with not encountered in the ground whole spices.

Very complete analyses of nearly all the spices of known purity, excepting mustard and turmeric, have been made by Winton, Ogden and Mitchell,[1] and the same analysts have made partial analyses of a large number of commercial mustard flours found on sale in Connecticut,[2] as follows:

TABLE I.

	Total ash.	Ether extract.		Reducing matters by acid conversion as starch.	Starch by diastase method.	Crude fiber.	Nitrogen × 6.25.
		Volatile.	Non-volatile.				
Maximum....	7.35	1.90	28.10	6.12	2.08	4.87	43.56
Minimum....	4.81	0.00	17.14	1.85	0.28	1.58	35.63
Average.....	5.99	0.56	20.61	4.33	1.07	2.58	39.57

Richardson[3] made the following analyses of whole seed flour, prepared by himself, without the removal of the fixed oil.

[1] Twenty-second Ann. Rep. Conn. Expt. Sta., 1898, p. 184.
[2] *Ibid.*, page 169.
[3] U. S. Dept. of Agric., Div. of Chem., Bull. 13, Part 2, page 181.

TABLE II.

	Water.	Ash.	Volatile oil.	Fixed oil.	Starch.	Crude fiber.	Albuminoids.	Undetermined.	Nitrogen.
White seed.....	5.57	4.29	0.97	33.56	0.00	5.40	28.88	21.33	4.62
White flour.....	3.33	5.23	1.84	34.83	0.00	9.05	25.56	20.16	4.09
Seed husk.....	6.17	4.99	0.55	28.12	0.00	9.50	23.44	27.23	3.75
California yellow	4.83	5.96	1.27	31.96	0.00	8.50	31.13	16.35	4.98
California brown	4.11	4.88	1.35	36.63	0.00	16.18	24.69	12.16	3.95
English yellow .	3.11	4.07	2.06	31.51	0.00	6.90	30.25	22.10	4.84
Trieste brown ..	4.62	5.61	0.63	39.55	0.00	10.84	25.88	18.87	4.14

Table III, which follows, shows the results of analyses made in the writer's laboratory of a number of the commoner varieties of mustard, both yellow and brown, acknowledgment being given to Mr. Arthur D. Smith for assistance in the analytical work. The mustard "flours" were prepared in the same manner as the commercial article, from seed separated as completely as possible from the hulls, and having the usual proportion of fixed oil removed by pressure. The "hulls" analyzed were some that had been separated from the seed in the ordinary process of sieving, in the manufacture of the flour, and afterwards reduced by grinding to a fine powder. The six varieties of whole seed examined were each ground directly in a porcelain power mill of the type known as a "chaser," yielding in each case a fine, oily mass, hardly suited for a commercial product, but very useful in serving as a basis for standards in that all the components of the seed were present in their natural proportions.

Methods of Analysis.—The methods of analysis employed were, in the main, those adopted provisionally by the Association of Official Agricultural Chemists.[1]

In the case of the brown seed, the developed volatile oil was determined by the following method:

Determination of Mustard Oil in Mustard Flour. Roeser's Method.[2]—Mix 5 grams of the sample with 60 cc. of water and 15 cc. of 60 per cent. alcohol, and let stand for two hours. Distil into a flask containing 10 cc. of ammonia, and, after about two-thirds of the solution have been distilled off, mix the ammoniacal distillate with 10 cc. of tenth-normal silver nitrate solution, and allow the mixture to stand for twenty-four hours, after which make up with water to 100 cc. Filter, and treat 50 cc. of the

[1] U. S. Dept. of Agric., Bur. of Chem., Bull. 65, Part X, "Spices."
[2] *Jour. Pharm. Chim.*, **15**, 361–364 (1902).

TABLE III.

	Moisture.	Total ash.	Water-soluble ash.	Ash insoluble in HCl.	Total ether extract.	Volatile ether extract.	Non-volatile ether extract.	Alcohol extract.	Total nitrogen.	Volatile oil.	Crude fiber.	Reducing matters by acid conversion as dextrose.	Reducing matters by diastase as dextrose.	On dry fat-free substance.					
														Alcohol extract.	Total nitrogen.	Total ash.	Crude fiber.	Reduc'g matters by acid conversion.	Reduc'g matters by diastase.
Mustard "flour" as prepared commercially :[1]																			
English brown	5.55	5.58	0.27	0.08	17.46	0.0	17.46	25.31	6.37	3.98	3.28	11.89	0.71	32.88	8.27	7.25	4.26	15.43	0.93
California brown	7.23	4.90	0.23	0.13	20.64	0.0	20.64	19.22	6.75	4.67	2.27	4.87	0.23	26.64	9.36	6.79	3.15	6.75	0.32
German brown	9.50	5.25	0 09	0 50	16.28	0.0	16.28	21.98	7.13	3.09	2.45	5.63	0 22	29.61	9.61	7.07	3.30	7 59	0.30
Av. of brown flours	7.43	5.24	0.19	0.24	18.19	0.0	18.19	22.17	6.75	3.91	2.67	7.47	0.39	29.71	9.08	7.04	3.57	9.92	0.52
German yellow	7.47	4.73	0.18	0.35	12.65	0 0	12.65	24.21	7.44	.....	1.87	6.12	0.23	29.93	9.20	5.85	2.31	7.57	0.28
California yellow	5.09	4.69	0.22	0.29	25.95	0.0	25.95	20.78	6.21	.....	2.21	5.75	0.00	30.13	9.00	6.81	3.20	8.34	0.00
Av. of yellow flours	6.28	4.66	0.20	0.32	19.30	0.0	19.30	22.49	6.83	.....	2.04	5 94	0.12	30.03	9.10	6.33	2.75	7.95	0.14
Average of all varieties of flour	6.96	5.03	0.19	0.27	18.59	0.0	18.59	22.30	6.78	.....	2.42	6.85	0.28	29.84	9.09	6.75	3.30	9.13	0.37
Mustard hulls as removed in preparation of flour:[2]																			
English brown	6.83	5.03	0.95	0.14	13.81	0.0	13 81	14.21	3.89	2.26	10.90	9.90	1.20	17.89	4.83	6.34	13.74	12.52	1.51
No. 2 brown	8.67	4.43	1.26	0.23	10.51	0 0	10.51	14.15	4.04	1.83	11.34	14.05	3.56	17.52	5.00	5.48	14.28	17.38	4.40
Av. of brown hulls	7.75	4.73	1.11	0.19	12.16	0.0	12.16	14.18	3.97	2.05	11.12	11.98	2.38	17.70	4.92	5.91	14.01	14.95	2.95
No. 1 yellow	6.46	4 56	2.33	0.05	7.03	0.0	7 03	11.07	3.03	.....	16.46	20.40	6 11	12.79	3.58	5.15	19.02	23.58	7.06
No. 2 yellow	5.36	4.65	1.91	0.22	6.63	0.0	6.63	10.46	3.22	.....	17.69	20.00	4.21	11.89	3.66	5.28	20.10	22.73	4.77
California yellow	9.12	4.59	1.78	0.05	7.79	0.0	7.79	8.51	3.60	.....	16.08	19.90	3.74	10 31	4.34	5.52	19.34	23.95	4.49
German yellow	8.46	4.66	1.80	0.04	6.17	0 0	6.17	8.07	2.90	.....	18.95	17.35	2 91	9.45	3.40	5.46	22.20	20.30	3.40
Av. of yellow hulls	7.35	4.65	1.95	0.09	6.90	0 0	6.90	9.53	3.19	.....	17.29	19.41	4.24	11.11	3.74	5.35	20.16	22.64	4 93
Average of all samples of hulls	7.48	4.65	1.67	0.12	8.66	0.0	8.66	11.07	3 45	.....	15.20	16.96	3.62	13.31	4.14	5.56	18.11	20.23	4.27
Whole ground mustard seeds :[3]																			
Bari brown	5.88	4.07	0.46	0.22	37.81	0.0	37.81	13.70	4.10	2.76	4.41	7.34	1.76	24.33	7.28	7.23	7.83	13.03	3.13
California brown	6.49	3.84	0.45	0.21	35.39	0.0	35.39	14 26	4.49	2.91	4.21	6 94	1.78	24.54	7.73	6.61	7.24	11.94	3.06
Av. of brown seeds	6.18	3.95	0.45	0.21	36.60	0.0	36.60	13.98	4.29	2.83	4 30	7.14	1.77	24.43	7.50	6.92	7.53	12.48	3.09
German yellow	6.69	4.34	0.63	0.56	27.19	0.0	27.19	17.75	5.09	0.0	4.87	9.35	1.45	26.85	7.70	6.61	7.36	14.44	2.19
Dutch yellow	5.93	4.83	0.73	0 33	30.84	0.0	30.84	14.98	4.12	0.0	6.53	10.06	1.82	23.69	6.51	7.64	10.33	15.91	2.87
English yellow	6.43	4.37	0.52	0.16	27.45	0.0	27.45	16.31	3.96	0.0	4.95	8.42	0.92	24.62	6.00	6.61	7.34	12.74	1.30
California yellow	6.82	4.05	0.57	0.42	28.64	0.0	28.64	16.11	4.72	0.0	5.28	9.60	1.15	24.96	7.31	6.28	8.18	14.88	1.78
Av. of yellow seeds	6.47	4.39	0.61	0.37	28.53	.....	28.53	16.29	4.47	.....	5.41	9.36	1.33	25.03	6.88	6.78	8.30	14.49	2.05
Average of all six samples of seeds	6.37	4.25	0.56	0.32	31.22	.....	31.22	15.50	4.41	.....	5.04	8.62	1.48	24.83	7.09	6.83	8.05	13.82	2.40

[1] Freed from hulls and with a portion of the fixed oil removed.

[2] These hulls necessarily have a little of the inner seed adhering thereto.

[3] Ground to a fine paste with full content of oil and hulls.

filtrate with 5 cc. of tenth-normal potassium cyanide solution. Titrate the excess of cyanide with the tenth-normal silver nitrate, using as an indicator a 5 per cent. solution of potassium iodide made slightly ammoniacal.

The percentage of mustard oil present is found by multiplying by 2 the number of cubic centimeters of silver nitrate solution taken up by the oil, and multiplying this product by the factor 0.3137.

Starch in Mustard.—Pure mustard contains absolutely no starch, yet mustard hulls of all varieties by the diastase method show considerable copper-reducing matter, which is not due to starch, and should not be attributed to it.

One sample of mustard hulls showed, by the diastase method, 7 per cent. of reducing matter, reckoned as dextrose,[1] in the moisture- and fat-free substance.

The material of the seed itself is comparatively free from such reducing matter, and when the separation from the hulls is complete, should show hardly a trace of reducing material by the diastase treatment. The mustard flours of the above table were practically free from contaminating starch, as shown by the microscope, the small amount of reducing action under the diastase treatment being undoubtedly due to the hulls which were left in them.

Hence it is often of considerable importance to ascertain whether the reducing matter is due to starch or to hulls, and this can readily be accomplished by a microscopical examination, which furnishes the very best, if not the only means of judging the character and extent of starch contamination, when the amount of starch is small.

In the standards recently adopted by the Secretary of Agriculture for certain food products,[2] standard ground mustard is defined as "containing not more than 2.5 per cent. of starch by the diastase method." It would seem as if some modification of this standard should be made.

From the fact that among the samples recorded in the above table 1.82 per cent. is the maximum of reducing material reckoned as dextrose found in the air-dry substance for mustard *ground from*

[1] The name dextrose is retained in place of the correct scientific name, *d*-glucose, because the former is always used in the publications of the A. O. A. C.—EDITOR.

[2] Office of the Sec. of Agric., Circular No. 10, p. 11.

the entire seed, and found by the microscope to contain only the minutest traces of contaminating weed starch, it would seem as if 2.5 per cent. of reducing matter in the air-dry powder was excessive.

Any actual starch present in ground mustard is due either to fraudulent admixture, or to the presence of starch-containing weed seeds common in some of the cheaper varieties of mustard seed. If contamination with foreign seed were to be legalized to the extent of 2.5 per cent. of actual starch, this would mean a percentage of foreign material far in excess of that figure, since starch is but one ingredient of these foreign seeds.

In view of the fact that starch is foreign to pure mustard, and that copper-reducing materials, other than starch, exist in mustard hulls under the diastase treatment, it would seem as if the standard should rule out more than mere traces of starch, as shown by the microscope. Furthermore, since the removal of the fat in more or less degree is customary, it would be better to express constants on the moisture- and fat-free basis, limiting the reducing matter by the diastase method in the moisture- and fat-free substance to, say, 2.5 per cent. not of actual starch, according to the present wording of the standard, but to "reducing matter reckoned in terms of dextrose," or, if desired, the equivalent "in terms of starch."

Typical of the cheap varieties of mustard high in foreign weed seed, which, it is claimed by manufacturers, cannot be removed from the mustard by sieving or by winnowing, are the Dakota mustard and some of the lower grade German seeds. By reason of the cheapness of these seeds there is constant temptation to use them. Such varieties were for obvious reasons not included in the above table, though the varieties analyzed were intended to cover a tolerably wide range. It is, in fact, questionable whether seed so highly contaminated with foreign material as the Dakota mustard should be allowed at all.

Following is the analysis of a sample of Dakota mustard flour, found by the microscope to be free from more than traces of hull tissue. It was found to contain over 3 per cent. of actual starch in the water- and fat-free substance, since, in the absence of hulls, practically all the reducing matter under the diastase treatment was due to starch.

TABLE IV.—DAKOTA MUSTARD FLOUR.

	Air-dry powder.	Moisture- and fat-free substance.
Moisture	7.42	....
Total ash	7.80	9.71
Water-soluble ash	0.46	0.57
Ash insoluble in hydrochloric acid	0.75	0.93
Ether extract	12.23	....
Alcohol extract	23.81	29.64
Total nitrogen	6.84	8.51
Volatile oil	3.76	4.68
Crude fiber	2.28	2.84
Reducing matter, by acid conversion, as dextrose	14.05	17.48
Reducing matter, by diastase, as dextrose	2.87	3.57
Reducing matter, by diastase, as starch	2.58	3.21

Numerous varieties of starch-containing weed seed were found in the whole Dakota mustard seed from which the above flour was prepared. Three of the most common varieties were picked out and analyzed for starch. One of these, evidently an inferior grade of broken wheat, was found to contain 70.93 per cent. of starch; another, a small circular seed, contained 70.65 per cent.; and a third, a small angular seed, contained 67.5 per cent. of starch, all three starch determinations being made by the diastase treatment.

Added Mustard Hulls.—Another method of producing a cheap mustard flour consists in the addition of ground mustard hulls. While it is true that the higher grades of mustard flour are deprived almost entirely of hulls, some are occasionally found that contain added hulls to an extent exceeding the amount of hulls in the whole seed. This practice should obviously be considered as a form of adulteration. Such an excess of hulls is rendered obvious by a microscopical examination, and may be confirmed by a chemical analysis. For this purpose certain additional standards would be helpful.

The main points of difference between hulls and seed substance of pure mustard are indicated chemically by such constants as the total nitrogen, the crude fiber and the reducing matter by diastase. The following table shows this in summarized form:

TABLE V.—IN THE WATER- AND FAT-FREE SUBSTANCE.

		Mustard flour. Per cent.	Mustard hulls. Per cent	Whole seed. Per cent.
Total nitrogen	Maximum	9.61	5.00	7.73
	Minimum	8.27	3.40	6.00
	Mean	9.09	4.14	7.09
Crube fiber	Maximum	4.26	22.20	10.33
	Minimum	2.31	13.74	7.24
	Mean	3.24	18.11	8 05
Reducing matter as dextrose, by diastase	Maximum	0.93	7.06	3.13
	Minimum	0.00	1.51	1.39
	Mean	0.37	4.27	2.40

One sample of commercial mustard flour comparatively free from starch, but condemned by the writer on account of added hulls, as shown unmistakably by the microscope, exhibited the following constants in the water- and fat-free substance:

	Per cent.
Total nitrogen	6.97
Crude fiber	7.69
Reducing matter as dextrose by diastase	2.20

In this sample the microscope showed the fragments of hull to clearly form the chief feature of the mass, largely exceeding the material of the seed tissue.

Suggested Standards.—Based on the above analyses, the following standards are suggested for ground mustard, expressed on the moisture- and fat-free substance: Reducing material by diastase treatment should not exceed 2.5 per cent., expressed as dextrose; crude fiber should not exceed 5 per cent.; and total nitrogen should not be less than 8 per cent. As shown by the microscope, the sample should be free from more than minute traces of starch, and should not exhibit an excess of hulls over seed tissue.

THE COMPOSITION OF TURMERIC.

BY ALBERT E. LEACH.

Received July 27, 1904.

TURMERIC (*Curcuma longa* of the family *Zingiberaceae*), while of chief interest to the analyst as an adulterant of other spices, possesses some value as a condiment in itself, forming, as it does, the chief ingredient of curry powder. Turmeric is a material especially adapted by its deep yellow color to intensify the color of mustard and ginger, especially when these spices are also

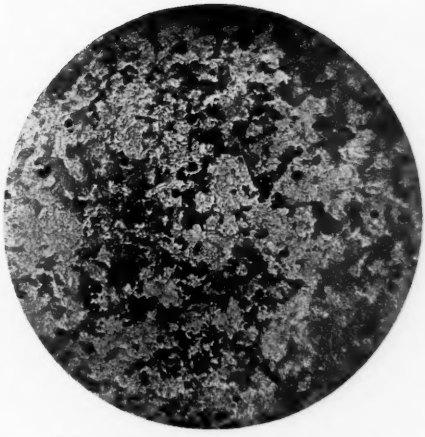


Fig. 1.—Dakota mustard flour, X 110. Dark spots show starch grains of foreign weed-seed, stained with iodine.

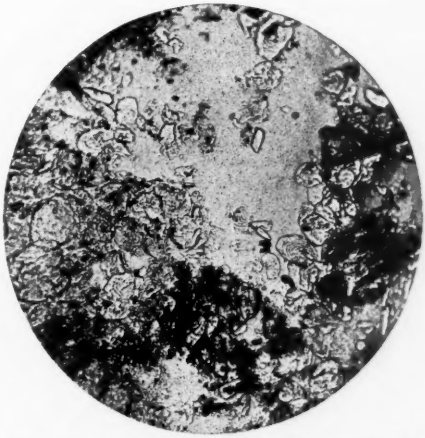


Fig. 2.—Powdered turmeric, X 110. Showing starch grains, fragments of cell tissue, coloring-matter, etc.

adulterated with the lighter colored cereal starches; hence it is very commonly found in these spices, both with and without other adulterants.

It is sometimes used, moreover, in small quantities in adulterated cayenne, mace, and various other spices, to counteract the colors of other dyestuffs, such, for instance, as ground redwood, which in itself would be too intense, if used as the sole artificial coloring agent in cayenne.

The chief ingredients of turmeric are starch, a slightly fluorescent, orange-yellow, volatile oil, a deep yellow coloring-matter (curcumin), soluble in alcohol, but insoluble in cold water, cellulose and a gum.

There are few, if any, records of the satisfactory analysis of turmeric, with the exception of two varieties of Bengal and Madras turmeric recorded in the recently issued 4th edition of König's *Nahrungs und Genussmittel*.[1]

The following are results of analyses made in the writer's laboratory of three varieties of turmeric commonly used in this country, the samples being ground in each case from large fragments of the root-stock.

Variety.	Moisture.	Total ash.	Ash soluble in water.	Ash insoluble in hydrochloric acid.	Total nitrogen.	Protein. N × 6.25.	Total ether extract.	Volatile ether extract.	Non-volatile ether extract.	Alcohol extract.	Crude fiber.	Reducing matters by acid conversion in starch.	Starch by diastase method.
China ..	9.03	6.72	5.20	0.11	1.73	10.81	10.86	2.01	8.84	9.22	4.45	48.69	40.05
Pubna..	9.08	8.52	6.14	...	0.97	6.06	12.01	4.42	7.60	7.28	5.84	50.08	29.56
Alleppi.	8.07	5.99	4.74	...	1.56	9.75	10.66	3.16	7.51	4.37	5.83	50.44	33.03
Average	8.73	7.07	5.36	...	1.42	8.88	11.17	3.19	7.98	6.96	5.37	49.73	34.21

MALT ANALYSIS.

By H. Aug. Hunicke.

Received July 13, 1904.

I. DETERMINATION OF EXTRACT.

While great quantities of malt are evaluated by inspection, it cannot be said that any considerable amount is purchased by analysis. The purchaser, while largely guided by the color, justly

[1] Vol. II., p. 1063.

observes more particularly the physical character of the endosperm. For the determination of the latter characteristics several simple tests are in use which can all be replaced, in a qualitative sense, by the simple biting test. However, where brewing operations are conducted on a rational basis it is preferable to determine quantitatively the extract-yielding properties of the malt.

The result of the mashing process depends in the main upon the quality of the malt used, but with the same grain results differ very widely with changes of temperature. This fact is so well established that one is not surprised to find that the first condition of uniformity, agreed to by chemists, was that of well defined working temperatures varied at definite intervals.

The method of analysis used is as follows: Fifty grams of malt are ground very finely into a copper beaker, 200 grams of water of 45° C. added and placed in a water-bath. The mash is allowed to remain at 45° for thirty minutes, when the temperature is raised 1° every minute, so that after twenty-five minutes the mash will be at 70° C., where it is kept for one hour. During the whole process, which lasts one hundred and fifteen minutes, the mash should be stirred. Upon completion the beaker is cooled down to about 10° to 15° C., placed on a balance and cold water added until the total weight of the contents is 450 grams. Stirring vigorously, so as to mix well, the whole is thrown upon a dry filter and allowed to drain into a dry flask. The first 75 cc. are returned and 150 cc. of the filtrate taken for a specific gravity determination. The German standard method prescribes that the first 100 cc. be returned to the filter and the *whole filtrate*[1] used for the determination of specific gravity. The method adopted by the subcommittee of the United States Brewers' Association differs from the above methods in that 250 cc. water are added at the outset. After the mash reaches 70° the iodine test is applied "every five minutes until inversion has taken place. The mash is then cooled to about 15° C. and its net weight is then increased to 450 grams by the addition of water. The mash is then carefully and thoroughly mixed and a *quantity of clear wort, sufficient for the saccharimeter determination,*[1] is filtered through a coarse filter."

Those who have had occasion to make many extract determinations of malt are conscious of the lamentable fact that the causes

[1] The italics are the writers. The bearing of these differences will be discussed more fully in another paper.

affecting the results are so manifold that even with the most conscientious work discordant results are easily obtained. So, for example, it is generally known that the physical character of the grain affects the yield very materially, so that one can, with certainty, predict a higher yield when the grain is mealy, while, on the other hand, a lower yield may be expected when the grain is hard and glassy, or else has failed to germinate. This difference of property finds expression in the extract determination of malt ground to varying degrees of fineness. The same grain will yield very nearly the same amount of extract, whether malted well or poorly, within reasonable limits, when ground to a very fine powder. When, however, it is ground coarsely the extract determination gives a higher yield the more thoroughly the malting process has rendered the grain soluble. It is for these reasons that some chemists are in the habit of making for each malt analysis at least two grindings, one being fine and the other coarse. The result of the finely ground sample indicates the amount of extract the grain might yield in practice with perfect malting, while the coarse grinding indicates the amount of extract obtainable in practice. The coarse grinding should be so adjusted as to give results comparable with those obtainable in the brewhouse.

It is evident that if the amount of extract yielded by any malt depends upon the degree of fineness to which it is ground, that in order to obtain comparable results in the laboratory, a mill of accurate construction must be used. The absolute lack of a laboratory mill, possessing the property of reliability as to the degree of comminution has left the matter of extract determination of malt in a state unworthy of an analytical method. However, since the newly designed Seck mill can be had it has become possible to produce a meal giving fairly uniform results. Unfortunately, the mill can be adjusted only to the coarser grades. Very fine grinding is impossible. The same firm has more recently built a mill for very fine grinding, which the writer has, however, not yet used.

After a season of experience with the first-mentioned mill, the writer observed, in making extract determinations, both from fine and coarse grindings, that the result of the coarse grinding did not vary as heretofore, apparently, with the physical properties of

the malt only, but seemed to vary also with the amount of water contained, the results being calculated to dry substance. This somewhat unexpected result was observed with sufficient regularity to make it comparatively certain. The writer, therefore, resolved to systematically investigate the effect of the variation of moisture on the yield of extract. For this purpose a sample of Wisconsin malt of the 1903 season was prepared by mixing twenty-four samples which had been analyzed during the previous winter and which varied in moisture from about 4 per cent. to nearly 6 per cent., the average being 4.64 per cent. The length of aerospire showed the following average results:

	Per cent.
0 to ¼	1.96
¼ to ½	0.08
½ to ⅔	0.67
⅔ to ¾	2.83
¾ to 1	66.46
1 and over	28.00

Otherwise, the physical properties may be said to have been of the average quality characteristic of Wisconsin grain when malted fairly well. Two determinations of extract had always been made, a finely ground one from a coffee-mill of French manufacture and a coarser one from the product of the Seck mill, set on the "25" mark. The former gave as an average result 70.64 per cent., extract, being 74.09 per cent., calculated to dry substance. The latter gave as an average result 66.60 per cent., extract, being 69.95 per cent., calculated to dry substance.

The mixed sample was treated with a current of fairly dry air for two days, which reduced the moisture to 4.44 per cent. At the same time the whole was thoroughly mixed, placed in a bottle, well stoppered and set aside for use. Portions of about 300 grams were filled into quart bottles and varying amounts of water added, the bottles being well corked, repeatedly shaken and allowed to stand a few days so as to allow the moisture to become uniformly diffused throughout the mass. It appears from the results given below that the preparation of the samples answered its purpose. This sample was marked "Malt I."

Six series of tests were made by varying the amount of moisture in the malt on the one hand and on the other hand grinding to 4° of fineness. The finest meal was ground in the coffee-

mill, already referred to, while three coarse grades, 0, 25, 50, were passed through the Seck mill, which was set at the marks indicated respectively.

SERIES I.

a. Moisture: — 4.46, 4.39, 4.48 and 4.42 = 4.44 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	70.82	68.92	67.14	54.32
Extract dry.....	74.11	72.12	70.26	56.84

b. Moisture: — 6.24, 6.23, 6.14 and 6.11 = 6.18 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	69.81	66.50	65.03	48.79
Extract dry.....	74.41	70.88	69.31	52.00

c. Moisture: — 7.89, 7.86, 7.85 and 7.79 = 7.85 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	67.58	64.78	62.82	45.40
Extract dry.....	73.34	70.30	68.17	49.27

d. Moisture: — 9.60, 9.49, 9.67 and 9.48 = 9.56 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	66.26	62.44	59.49	40.55
Extract dry.....	73.26	69.04	65.78	44.84

e. Moisture: — 11.12, 10.95, 11.33 and 10.69 = 11.02 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	64.87	59.35	45.61	31.19
Extract dry.....	72.90	66.70	51.26	35.05

f. Moisture: — 12.92, 12.65, 12.82 and 12.88 = 12.82 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	64.20	59.29	52.29	31.94
Extract dry.....	73.64	68.01	59.98	36.64

It seemed desirable to extend the investigation to unground malt and accordingly one test of each of the watered samples of "Malt I" was made with the following results:

SERIES II.

Moisture. Per cent.	Extract. Per cent.	Extract, dry. Per cent.
4.44	5.30	5.55
6.18	5.31	5.66
7.85	5.56	6.03
9.56	5.42	5.99
11.02	5.58	6.27
12.82	5.46	6.26

These values should all be equal, which is practically the case. A slight increase of extract with increase of water is, however, discernible, though not too much value should be attached to this observation because the differences are evidently not greater than would be expected from the nature of the process.

Another sample was similarly prepared. Being of similar origin as the first sample, the results are directly comparable. This was marked "Malt II."

SERIES III.

a. Moisture: — 4.43, 4.46, 4.51 and 4.41 = 4.45 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	70.96	69.87	68.06	51.24
Extract dry.....	74.26	73.12	71.23	53.63

b. Moisture: — 6.36, 6.26, 6.32 and 6.27 = 6.32 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	69.25	67.59	65.58	65.61
Extract dry.....	73.91	72.13	69.99	70.02

c. Moisture: — 8.06, 8.00, 7.97 and 7.91 = 7.99 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	68.33	65.73	63.10	39.85
Extract dry.....	74.26	71.66	68.58	43.31

d. Moisture: — 9.70, 9.69, 9.66 and 9.69 = 9.69 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	66.75	63.74	59.13	34.04
Extract dry.....	73.91	70.58	65.47	37.69

e. Moisture: — 11.56, 11.45, 11.40 and 11.41 = 11.45 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	65.27	61.46	53.95	27.24
Extract dry.....	73.71	69.41	60.70	30.76

f. Moisture: — 13.29, 13.21, 13.24 and 13.14 = 13.22 per cent. average.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	64.46	59.06	48.21	22.10
Extract dry.....	74.28	68.06	55.55	25.47

In the two principal series, I and III, the decrease of yield of extract with increase of moisture becomes so pronounced that there can be little doubt of its reality. While the finest grades indicate a certain degree of uncertainty in this respect, a general agreement is, however, observable. The apparent discrepancy in the results containing 12.82 per cent. and 13.22 per cent. water,

respectively, is due to the difficulty of passing malt of such high water content through the coffee-mill without subjecting it to a long-continued grinding action, the damp particles adhering at times. The coarser grades all prove the rule. This comes out very clearly in Series III, where special care was exercised in stirring uniformly at equal intervals.

There may be several reasons for this variation of yield with variation of water content. The amount of moisture in a sample of malt affects the degree of fineness obtained with any given mill by making the individual grains softer and, therefore, more yielding, causing them, upon compression, to behave much like a rubber bag containing water, the more so the higher the water content. Such softened grains yield very little dust in the process of grinding. The starch cells are not disrupted to any great extent when the water content is high. Just to what extent a higher water content will affect the yield of extract will always depend more or less upon the quality of the malt. The latter always affects the degree of fineness resulting from any disintegrating process. Evidently then the degree of fineness of the ground product depends upon the brittleness or lack of coherence of the internal structure of the grain. Anything which decreases the brittleness either by causing greater toughness or greater softness, which may either be due to an increased toughness of the starchy content or softening of the cell wall and their contents, will lower the yield of extract.

The lower yield of extract from increased percentage of water may perhaps also be accounted for in a measure by the increased dilution of the charge, thereby retarding the reaction both as to time and quantity. This is shown by the following results:

"Malt I" was used. It was ground in the coffee-mill to the finer grade and four tests made by varying the charge of malt; otherwise all conditions remained as usual. The amounts of malt taken were 50, 40, 30 and 20 grams respectively, giving:

SERIES IV.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	71.04[1]	70.39	70.07	67.87
Extract dry ...	74.34[1]	73.65	73.31	71.02

[1] Strictly these two figures should be 70.82 per cent. and 74.11 per cent. respectively as given in Series I. This difference corroborates the repeatedly observed variation of the fine grindings from the coffee-mill which is not absolutely reliable in the uniformity of results.

This certainly shows that the yield of extract is lowered to an appreciable extent by dilution and within the errors of the method it would almost appear to explain the decreased yield of Series I and III, but it is by no means quite clear whether dilution can account for all of the loss of yield, especially as results are wanting on coarser grades. The entire supply of the prepared sample of malt having been used, it was impossible to extend the research to the coarser grades.

The results given thus far prove conclusively the relation of yield to water content. The various results given are by no means as concordant in other respects as might be desired. It is hardly possible to enumerate all the various causes tending to disturb the results. The writer has set out to discover some of the many influences affecting the results. Of course, the matter of working temperatures can be dismissed at once, as under all circumstances great care must be observed in maintaining the prescribed temperatures. This, however, is by no means easily accomplished and, therefore, remains as a variable factor to some extent. But one factor which appeared to need some inquiry was that of the influence of stirring. To investigate this, three series of extract determinations were made.

Samples of "Malt I" were ground in the Seck mill set at 0, 25 and 50 marks respectively. The first sample was treated in four different ways, the first being stirred every minute, the second every five minutes, the third every fifteen minutes and the fourth not at all.

SERIES V.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	55.68	54.00	53.81	53.43
Extract dry.....	58.27	56.57	56.31	55.91

The second sample was also treated in four different ways: The first was stirred during the entire time of mashing, one hundred and fifteen minutes, the second during the first eighty-five minutes, the third during the first fifty-five minutes and the fourth during the first thirty minutes.

SERIES VI.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	56.60	55.65	55.96	53.73
Extract dry.....	59.23	58.24	58.56	56.23

The third sample was again treated in four different ways, corresponding to those of the first sample.

SERIES VII.

	Fine. Per cent.	0. Per cent.	25. Per cent.	50. Per cent.
Extract	67.31	67.09	67.45	67.03
Extract dry....	70.44	70.21	70.58	70.14

It will be observed that for coarse grindings a very perceptible decrease of yield is obtained when the mash is not stirred at all, and stirring even at intervals of five minutes will not give results as high as stirring every minute. So also does it become apparent from the results given that good stirring during the rising temperature is most essential. In finer grades of grindings the differences of yield, due to want of stirring, do not become great. In fact, it might be inferred from the results that very finely ground malt will yield up its entire extract without stirring at all or at most merely occasionally stirring. It follows from this that in the process of extract determination the mash should be stirred occasionally when working on finely ground malt, but when the test is applied to coarsely ground malt a well regulated method of stirring should be adopted. After the method of making two extract determinations of malt becomes more general it will be found necessary to agree on a uniform method of stirring. This applies particularly to the coarser material. It should not be inferred that the more vigorous the stirring the better the result. The danger lies rather in the opposite direction. The greater yield on the coarser grindings from a more vigorous stirring may be largely due to the disintegrating effect of the stirring, which must be greater with the coarsest grades of malt and the information sought by coarse grinding may thus be obscured.

Such disturbing factors as lack of uniformity of samples must always be an element of uncertainty in all extract determinations. Even with thorough mixing the variability of the individual grains and their weight, as compared with the charge, probably makes it impossible to expect a greater accuracy than 0.1 per cent., other errors being eliminated, for 1 grain of malt weighs about 0.025 gram, which, on a charge of 50 grams, is 0.05 per cent.

A loss, perhaps almost unavoidable, is that due to the formation of dust in the process of grinding and that, of course, applies

more particularly to the finer grades. It has been suggested to add from 1 to 3 grains of malt in excess of the 50 grams, taken for the test to cover the losses due to brushing off the parts of the mill. While this suggestion is a good one in a general way, it cannot be applied with equal justification to all degrees of fineness or malts of high percentage of moisture. The better the malt and the lower the percentage of moisture the greater the loss from the formation of dust. Another method practiced to some extent is to weigh a charge somewhat in excess of 50 grams, to grind the latter and weigh the exact amount afterward. This would appear acceptable if it were not for the hygroscopic properties of many samples of malt, more particularly those which have been dried to a high degree. The method is recommended by the German conventional method for fine grinding; for the coarser grindings 50 grams are weighed and then ground. If the loss due to the formation of dust is variable, there is no justification for adding a constant correcting factor in the form of one or more grains, hence this method is objectionable.

The rate of grinding must affect at least the coarser grades, as the energy applied to each grain as it drops in between the rolls depends upon the speed of the rolls. The greater the speed of grinding the greater is the energy applied to the grain; the greater the latter the greater the comminution. It follows from this that at least for the coarser grades the mill should be adjusted to some standard speed, at least approximately, and that the feeding hopper be filled and grinding then begun with well regulated speed.

A source of error lies in the method of filtration. It is well known that the first drippings of the malt indicate a lower density, due to the adsorption of the extract by the filter-paper. This error is very generally obviated by returning the first runnings to the filter. Just to what extent this phenomenon of separation of solvent and solute during filtration affects the results of extract determination will be the subject of another paper.

ST. LOUIS, MO.

[CONTRIBUTION FROM THE LOUISIANA SUGAR EXPERIMENT STATION.]

THE HYDROLYTIC PRODUCTS OF SUGAR-CANE FIBER.

BY C. A. BROWNE, JR.

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OWING to the greater demands upon the chemist of problems dealing solely with the workings of the sugar-house, the study of the insoluble constituents of the sugar-cane has been, in the past, more or less neglected. It is only since the utilization of bagasse for paper-making has begun to attract attention that the chemical nature of sugar-cane fiber has assumed more than theoretical interest.

Cross and Bevan, in their work on cellulose (page 220), state that the fiber aggregates of the sugar-cane "are largely made up of pectocelluloses, with a greater or less proportion of lignocelluloses But the constitution of these non-cellulose constituents are, as yet, quite unknown; and we have, therefore, none but the general basis of classification."

More specific information concerning the constituents of cane-fiber is given by Prinsen Geerligs.[1] This authority, who has made a special study of the sugar-cane in Java, states that the fiber of mature cane contains about 50 per cent. of cellulose and 30 per cent. of cane-gum, or *xylan*. The latter constituent was obtained from the fiber in an impure state by extraction with cold 5 per cent. caustic soda, and precipitation with acetic acid and alcohol. The gum possessed a specific rotation of —80° and yielded, on hydrolysis with acid, 79 per cent. of sugar. Crystals of the sugar thus obtained gave a specific rotation of +20°; xylose was, therefore, probably present and also "probably another sugar with a higher rotatory power, perhaps arabinose or *d*-glucose proceeding from the hydrolysis of cellulose."

During the past year investigations have been conducted at the Louisiana Sugar Experiment Station upon the composition and chemical properties of cane-fiber, especially since the commercial utilization of this fiber, in a number of ways, is now giving promise of success. In these investigations the hydrolytic action of hydrochloric, sulphuric and nitric acids, and of caustic soda have each been studied, but as the full results of this work would form too compendious a contribution, the present article will be limited

[1] "Observations on Bagasse," *Sugar Cane*. **30**, 91.

to a consideration of those products obtained by digesting cane-fiber with dilute caustic soda.

MICROCHEMICAL REACTION OF CANE-FIBER.

The tissues of the sugar-cane resemble very closely those of maize, sorghum, and many other monocotyledonous plants and consist of the pith (the parenchyma or fundamental tissue), the fibrovascular bundles, and the shells or rind. The reactions of thin sections of a cane stalk with various reagents are given in Table I. The sections were prepared with a microtome and then washed in cold water to remove sugars.

TABLE I.

	Pith.	Bundles.	Rind.
Chloride of zinc and iodine	No color	No color	No color
Phloroglucin and hydrochloric acid	Pink	Red	Red
Mäule's permanganate test	Pink	Red	Red
Aniline sulphate	Pale yellow	Yellow	Yellow
Ferric ferricyanide	Light blue	Dark blue	Dark blue
Chlorine water	Yellow	Orange	Orange.

The absence of any reaction with chloride of zinc and iodine indicates a complete combination of the cane cellulose with other substances. After boiling the sections with dilute caustic soda and washing, the blue coloration, characteristic of cellulose, was obtained without difficulty.

The reaction with phloroglucin and hydrochloric acid, formerly supposed to be indicative of lignin and later regarded as a test for pentosans, has been shown by Czapek[1] to be produced by an aldehyde body, *hadromal,* found occurring in nearly all lignified tissue.

Mäule's[2] permanganate test is regarded by its author as indicative of lignin groups alone. Since the details of this valuable test are not generally known, a short description may be allowable. The sections for examination are placed for five minutes in a 1 per cent. solution of potassium permanganate; they are then washed in water and decolorized with hydrochloric acid. After washing to remove acid, the sections are placed in ammonia water, when the lignified tissues will be colored a deep red.

The reactions of the cane tissues with aniline sulphate, ferric

[1] *Ztschr. physiol. Chem.*, **27**, 141 (1899).

[2] Mäule: "Das Verhalten verholzter Membranen gegen Kaliumpermanganat," *Beiträge zur wissenschaftl. Botanik.*, Band IV.

ferricyanide and chlorine water point, as does the previous test, to a higher degree of lignification in the fibrovascular bundles and rind, than in the pith, although it must be noted that the very thin character of the cell walls in the fundamental tissue tends to diminish greatly the intensity of the color reactions in this region.

SEPARATION AND COMPOSITION OF THE TISSUES OF SUGAR-CANE.

A mechanical separation of the different tissues of the cane was accomplished only with considerable difficulty, the isolation of the bundles from the pith being especially arduous. The following analyses were performed upon a mature stalk of the Louisiana purple variety of cane:

	Pith. Per cent.	Bundles. Per cent.	Rind. Per cent.
Whole cane (3 analyses)	2.39	1.81	5.51
Dry fiber	24.66	18.60	56.74

A proximate analysis of the above tissues is given below. The results were calculated to a moisture-free basis.

TABLE II.

	Pith. Per cent.	Bundles. Per cent.	Rind. Per cent.
Ash	1.68	3.58	1.64
Fat and wax	0.41	0.72	0.98
Protein	1.94	2.00	2.19
Cellulose (method of Cross and Bevan)	49.00	50.00	51.09
Pentosans (furfuroids	32.04	28.67	26.93
Lignin (by difference)	14.93	15.03	17.17

With the exception of ash the results for the different tissues show a certain regularity, the bundles standing intermediary between the pith and rind. The analytical data confirm, in a general way, what was indicated by the microchemical tests, *viz.*, that we have in the pith a minimum and in the rind a maximum degree of lignification.

DIGESTION OF CANE-FIBER WITH CAUSTIC SODA.

Preparation of Material.—Several kilos of finely cut bagasse were washed with successive portions of cold water until all traces of sugars were removed. The mass was then allowed to soak over night in cold 2 per cent. hydrochloric acid, to dissolve as much mineral matter as possible. After pressing, the fiber was washed free from acid and dried.

Method of Digestion.—Two hundred grams of the purified fiber were digested eight hours with 3 liters of 5 per cent. caustic soda. The reaction was carried out in a large flask immersed in a boiling water-bath. After terminating the reaction, the contents of the flask were cooled and the dark brown alkaline liquid filtered through a large Büchner funnel. The residual pulp was washed several times with small quantities of cold water, and the combined filtrate and washings set aside in a tall cylinder for several days to allow suspended impurities to settle. The pulp was rewashed with hot water until free from alkali, and then with strong alcohol. After drying, an impure cellulose of light straw color was obtained, which in weight amounted to 80 grams, or 40 per cent. of the original bagasse. The soda-liquor and dried pulp were each separately examined.

EXAMINATION OF SODA-LIQUOR FROM CANE-FIBER.

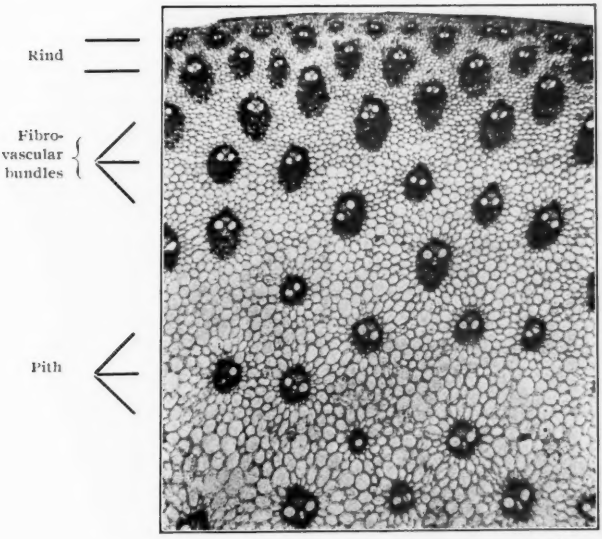
For the precipitation of the extractive matter removed by caustic soda from cane-fiber, several methods were tested, among them the use of acids, of a mixture of acids and alcohol, and the use of alcohol alone. The latter was finally adopted as the first precipitating agent, since it effected a complete separation of the hemicelluloses without precipitating any of the lignin. With methods which involve the use of acids it was found that the pentosans and lignin were precipitated together and a separation of these two groups of constituents was not secured.

I. PRECIPITATION OF CANE-GUM (PENTOSANS) FROM SODA-LIQUOR.

The original method of Tollens[1] and Wheeler for preparing wood gum was followed with a few slight modifications. The clear soda-liquor was filtered through parchmentized paper from all sediment and evaporated to one-third of the original volume. Double the quantity of pure 95 per cent. alcohol was then added, when a flocculent yellowish colored coagulum was thrown out. After settling, this was filtered off on parchmentized paper through a Büchner funnel and the precipitate washed with alcohol until the washings were colorless. The alcoholic filtrate was preserved for subsequent examination.

The precipitate upon the filter was transferred to a large porcelain mortar and thoroughly ground up with an excess of alcoholic

[1] *Ann. Chem.* (Liebig), **254**, 304.



Transverse section of sugar-cane, highly magnified. Showing different tissues.

hydrochloric acid to break up all alkaline compounds of the gums. The residue was again filtered off and thoroughly washed, first with 80 per cent. alcohol till free from acid, then with 95 per cent. alcohol, and finally with a little ether. The product thus obtained was dried for several weeks over concentrated sulphuric acid, after which it was ground, when it was obtained in the form of a very light powder, almost white in color. Weight of product, 50 grams, or 25 per cent. of the original fiber.

Properties and Composition of Cane-gum.—The cane-gum, as above prepared, was difficultly soluble in hot water, to which it gave a milky opalescent appearance. In dilute solution of caustic alkali it easily dissolved to a clear brown solution, from which it was reprecipitated by adding acids. One-half gram of the gum, dissolved to 200 cc. in a 0.2 per cent. solution of sodium hydroxide, gave a reading of —0.6° Ventzke in the 100 mm. tube. The specific rotation of the gum would then be

$$[\alpha]_D = \frac{-0.6 \times 0.3468 \times 200}{0.5 \times 1} = -83.2.$$

Dry distillation of the gum in a closed tube produced dense vapors of furfural. Large quantities of furfural were also obtained on distilling with hydrochloric acid. One-half gram of gum gave, by the method of Kröber and Tollens, 0.4280 gram of furfural-phloroglucide = 44.88 per cent. furfural = 76.43 per cent. pentosans. The gum contained 12 per cent. ash (mostly sodium chloride). Cellulosic gummy products, derived from cane-cellulose, were also present in small amounts, as was shown by microchemical tests with zinc chloride and iodine.

Hydrolysis of Cane-gum with Hydrochloric Acid.—The process was carried out according to Councler's[1] method for wood-gum. Twenty grams of cane-gum were heated with 500 cc. of 4 per cent. hydrochloric acid on a boiling water-bath for ten hours. The reaction was carried out in a flask provided with a condensing tube. At the end of the hydrolysis the hot solution was treated with an excess of lead carbonate and allowed to stand in the cold over night. The liquid was then filtered from the deposit of lead chloride and carbonate, and evaporated to about 80 cc. The syrup thus obtained was shaken up with 500 cc. of strong alcohol

[1] Councler: "Verzuckerung von Holzgummi mittelst Salzsäure," *Chem. Ztg.*, **16**, [2], 1719 (1892).

and 50 cc. of ether and the precipitate of gummy matter (reversion products) allowed to subside. The solution was then filtered and evaporated to about 50 cc. A light straw-colored syrup was thus obtained, which was set aside for crystallization in a cool place over sulphuric acid.

Separation and Identification of Xylose from Cane-gum.—Crystals began to appear in the syrup at the end of a few hours. These, when examined under a micropolarizer, were seen to be optically active. After two days the entire syrup had set to a crystalline mass; this was stirred up with strong alcohol and filtered off on a suction plate. After washing with alcohol and ether a residue of nearly white crystals were obtained, which, on drying, weighed 5.342 grams = 26.71 per cent. of the original gum. The product was recrystallized from hot alcohol, using bone-black, when it was obtained in a pure white condition.

A solution of the crystals in water reduced Fehling's solution strongly. Heating with hydrochloric acid gave off strong odors of furfural; warming with phloroglucin and hydrochloric acid produced a brilliant red coloration. These reactions indicate a pentose sugar. To determine the specific rotation, 0.8648 gram of the carefully dried sugar was dissolved in water to 25 cc. and polarized in a 200 mm. tube, using a Schmidt and Haensch triple-shadow saccharimeter. Strong multirotation was observed. The following series of observations was made:

Time after solution. Minutes.	Polariscope reading. Ventzke.	Specific rotation, $[\alpha]_D^{16°}$.
10	+14.8	+74.2
20	11.0	55.1
30	8.6	43.1
40	7.1	35.6
50	6.3	31.6
60	5.5	27.6
70	5.0	25.1
80	4.7	23.6
90	4.5	22.6
Hours.		
2	4.1	20.6
3	4.0	20.0
12	3.7	18.5

The constant specific rotation of +18.5 agrees with that of *l*-xylose. The calculated value for *l*-xylose for the above concentration, according to Tollens' formula $[\alpha]_D = 18.095 +$

0.06986 *p*, is 18.33. The initial specific rotation of *l*-xylose, as calculated from the data in the above table, would be about +100, which agrees with the figure of Lippmann.[1]

As additional identifications of the above sugar, an osazone was formed with phenylhydrazine, which melted at 157°-158° C. and which polarized in a 1 per cent. alcoholic solution —0.44° Ventzke. These properties agree with those of *l*-xylose-phenyl-*α*-azone. By oxidizing a solution of the sugar with bromine in presence of cadmium carbonate, characteristic crystals of the double xylonate and bromide of cadmium, $C_5H_9O_6CdBr + H_2O$, were obtained.[2]

Separation and Identification of Arabinose from Cane-gum.—The mother-liquor obtained after separating the xylose was purified with alcohol and ether, and set aside for a second crystallization, but the crop of new crystals was so small that the presence of remaining quantities of xylose was disregarded and examination was made for arabinose. For the separation of this and other sugars in mixtures, use has been made of the recently studied substituted hydrazines, such as benzyl-phenyl-hydrazine, diphenyl-hydrazine, methyl-phenyl-hydrazine, etc., reagents of growing importance in the analysis of sugars. In the present instance the first-named hydrazine was employed.

The syrup was diluted with twice its volume of strong alcohol and to this was added a solution of 10 grams benzyl-phenyl-hydrazine in 20 grams of 95 per cent. alcohol. After standing a few hours in the cold, needle-shaped crystals began to form and on stirring, the solution rapidly thickened with the formation of a dense crystalline deposit. This was filtered off and washed on a suction plate with 20 cc. of 80 per cent. alcohol. A nearly white product resulted, which was further purified by recrystallizing from boiling alcohol, using animal black. 1.6 grams of a snow-white compound were obtained, which melted sharply at 169°-170°. The melting-point of *l*-arabinose-benzyl-phenyl-hydrazone is 170°.

For the separation of sugars from their hydrazones the practice of decomposing the latter with concentrated hydrochloric acid has, at present, given place almost entirely to the method of digesting an alcoholic solution of the hydrazone with formaldehyde

[1] Lippmann's "Die Chemie der Zuckerarten," 3 Auflage, p. 128.
[2] "Bertrand's Reaction," *Bull. Soc. Chim.*, **3**, [5], 557.

or benzaldehyde. The writer has employed both of the above aldehydes with equal success, but has found formaldehyde preferable in most cases, since the process is more easily controlled.

1.2 grams of the hydrazone, obtained from the cane-gum, were dissolved in a small flask in 15 cc. of boiling alcohol and the solution treated with 3 cc. of formaldehyde (40 per cent. solution). The flask was closed with a condensing tube and the contents kept in gentle ebullition for an hour. After cooling, a yellowish colored oil (formal-hydrazone) separated and no crystallization of undecomposed hydrazone occurring, the process of decomposition was judged complete. After filtering from the oily deposit, the clear filtrate was shaken out several times with ether and the aqueous solution filtered and evaporated to 5 cc.; the syrup was set aside in a cool place over sulphuric acid and in a few hours solidified to a crystalline mass. The crystals were ground up with 90 per cent. alcohol and washed by decantation, first with strong alcohol and then with ether. 0.35 gram of a pure white sugar was obtained.

To determine the specific rotation 0.3392 gram of the carefully dried sugar was dissolved to 10 cc. and polarized in a 100 mm. tube. Strong multirotation was noted. The following series of readings was obtained:

Time after solution. Minutes.	Polariscope reading. ° Ventzke.	Specific rotation, $[\alpha]_D^{20°}$.
10	16.0	+163.5
15	15.0	157.3
20	14.0	143.1
40	11.5	117.5
Hours.		
2	10.4	106.3
4	10.2	104.2
20	10.2	104.2

The constant specific rotation of +104.2 agrees with that of *l*-arabinose. The values given by Landolt[1] range from +103.9 to +105.4. The initial specific rotation of arabinose, as calculated from the data above, would be about +190, which agrees with the figure of Lippmann.[2]

The results of the experiments show that both xylose and arabinose are formed by the hydrolysis of cane-gum. The mother substances of these sugars, xylan and araban, make up, as was

[1] Landolt's "Das optische Drehungsvermögen," 2 Auflage, p. 512.
[2] Lippmann's "Die Chemie der Zuckerarten," 3 Auflage, p. 62.

shown, nearly 80 per cent. of the cane-gum, in the probable ratio of 4 to 6 parts xylan to 1 of araban.

A method has been devised by Salkowski[1] for the separation of xylan from other carbohydrates, based upon its precipitation from alkaline solution with Fehling's reagent. The gelatinous xylan copper compound is strained off, washed with a little water, and then rubbed up with dilute hydrochloric acid. Alcohol is then added and the gum washed and dried in the usual way. In case much araban is present the process of purification is repeated.

The method of Salkowski was applied to a quantity of the gum obtained from sugar-cane fiber. The yield of xylan after two precipitations with Fehling's solution was only 36 per cent. of the original gum, showing that the process of purification is attended with great loss. The final product was nearly white and gave, on analysis, the following results:

Specific rotation $[\alpha]_D = -88.8$.
Ash = 5.16 per cent.
Xylan ($C_5H_8O_4$) = 80.15. (Furfural = 51.72 per cent.)
Undetermined, 14.69.

The above gum was hydrolyzed with dilute hydrochloric acid, and an examination of the sugars formed failed to detect the presence of arabinose. We may conclude, therefore, that all araban was eliminated in the process of purification. According to Salkowski, xylan, as above prepared, exists as a hydrate $(C_5H_8O_4)_2 + H_2O$; recalculating the xylan in the above table to this formula would give 85.6 per cent. There still remains, however, nearly 10 per cent. of undetermined matter, consisting probably of a hexane carbohydrate, $(C_6H_{10}O_5)_n$, formed by the action of the alkali upon the cane-cellulose (cellulose gum). Oxidation of the gum with nitric acid gave large amounts of oxalic acid, but no mucic acid could be detected; galactan groups were, therefore, absent. It should be noted, however, that in the fiber from immature cane, galactan has been found in small amounts (0.72 per cent.).

II. PRECIPITATION OF LIGNIN FROM SODA-LIQUOR.

The alkaline filtrate from the cane-gum was evaporated until all alcohol was expelled and then acidified in a large flask with

[1] Salkowski: *Ztschr. phys. Chem.*, **34**, 162; **35**, 240.

dilute sulphuric acid. A dark brown precipitate was thrown down which, on heating, collected together as a sticky, gummy mass. After cooling, the clear liquid above the deposit was filtered off and preserved for subsequent examination. The gummy deposit, which had hardened to a solid cake, was readily detached from the walls of the flask. Any adherent particles were dissolved in dilute caustic soda, reprecipitated in a small beaker with sulphuric acid and combined with the main portion. The product thus obtained, when warmed in the moist condition, softened into a gummy plastic mass, but when cold hardened into a brittle resinous body, which was easily reduced to a powder. After washing with cold water to remove all traces of acid, the product was dried, first over sulphuric acid and then at 90°. Weight of material, 21.56 grams, or 10.78 per cent. of the cane-fiber.

Properties of Lignin Precipitate.—The product obtained, as above described, formed a brown-colored powder, insoluble in water and alcohol, but easily soluble in alkaline solutions, from which it is reprecipitated by acids, but *not* by alcohol. Heating with hydrochloric acid gave not the slightest trace of furfural, showing the complete absence of pentosans. Dry distillation in a closed tube produced large quantities of tarry products and oily acid compounds of a phenol nature.

Chlorination Product of the Lignin Precipitate.—By subjecting jute and other fibers to the action of free chlorine Cross[1] and Bevan have isolated a well defined chlorination product, lignone chloride, to which they have given the formula $C_{19}H_{18}Cl_4O_9$. A product very similar to the above was prepared from the lignin residue obtained from cane-fiber.

Five grams of the lignin precipitate were dissolved in dilute sodium hydroxide and the solution saturated with chlorine gas. The solution gradually changed in color from a dark brown to a deep yellow and was finally rendered turbid through the precipitation of yellowish colored flakes. The contents of the beaker were then heated to boiling and hot alcohol added with constant stirring until complete solution was effected. The acid solution was then filtered into a large beaker of water, when a flocculent lemon-colored precipitate was thrown out. After standing several hours the clear liquid was decanted and the precipitate filtered

[1] Cross and Bevan's "Cellulose," page 135.

upon a hardened paper through a Büchner funnel. The precipitate was washed thoroughly with cold water to remove all acid, when it was removed from the filter and dried.

The chlorination product, as above prepared, formed a yellowish powder, insoluble in water, but easily soluble in hot alcohol, acetone and glacial acetic acid; chloroform and carbon disulphide exerted no solvent action. Repeated attempts were made to crystallize the body, but without success. A solution of the compound in alcohol is not readily reprecipitated by pouring into water unless a certain amount of free acid is present.

A determination of chlorine in the compound gave 27.98 per cent. Cross and Bevan obtained for the lignone chloride from jute 26.83 per cent. The two compounds from their similarity in composition and reaction are undoubtedly one and the same.

III. ACETIC ACID FROM SODA-LIQUOR.

The acid filtrate from the lignin precipitate was made up to a liter, and 50 cc. of the solution (10 grams fiber) were subjected to distillation in a current of steam. 87.1 cc. of N/10 barium hydroxide were required to neutralize the distillate. The neutralized solution was evaporated and the barium salt obtained in crystalline form. The product was dried and analysis showed it to consist entirely of barium acetate. Per cent. of barium found = 53.64. Theoretical for barium acetate, 53.79 per cent.

The amount of acetic acid found in the soda-liquor would equal 5.23 per cent. of the original fiber.

Examination of Soda Cellulose from Cane-fiber.—The dry cellulose obtained by digesting cane-fiber with caustic soda amounted to only 42 per cent. of the original fiber. This low yield of cellulose, compared with a determination of cellulose by the chlorination method, is to be explained by the solvent effect of the soda, particularly upon the cellulose of the pith. The following figures show the relative resistance of the different tissues of the cane to various chemical treatments.

	Pith. Per cent.	Bundles. Per cent.	Rind. Per cent.
Cellulose by chlorination (Cross and Bevan)····	49.00	50.00	51.09
" " Weende method (treatment with 1.25 per cent. H_2SO_4 and 1.25 per cent. NaOH)	42.86	48.64	54.76

The results show a large amount of cellulose dissolved from the

pith by the Weende method—a circumstance due largely to the very spongy and cellular character of the pith, which renders it more easily attacked than the rest of the fiber. The pith cellulose, after the removal of other cellular groups, appears, moreover, to exist in an extremely hydrated, almost colloidal, form, which is an additional explanation of its greater susceptibility to chemical treatment. These facts have an important bearing upon the utilization of cane-fiber for paper-making, since a chemical treatment necessary for the proper re-solution of the shells would result in a large loss of pith. To prevent this loss a process[1] has been patented consisting in a preliminary separation of the pith from sugar-cane, corn-stalks, etc., before digesting the shells. The pith is not fibrous and has no felting properties, yet paper made from it possesses the quality and strength of parchment; this is to be explained by the intense cementation which the hydrated cellulose undergoes during the process of dehydration.

Reactions of Soda Cellulose.—The cellulose prepared from cane-fiber by the soda process was by no means pure. Microchemical tests by Mäule's method showed lignin to be present and pentosans were also indicated by heating the fiber with hydrochloric acid and testing the filtered solution with phloroglucinol. A distillation with hydrochloric acid gave 5.07 per cent. furfural, a considerable portion of which, however, must have resulted from the action of the acid upon oxycellulose.[2]

Hydrolysis of Soda Cellulose.—Twenty grams of the finely divided cellulose were treated in the cold with 50 cc. of 90 per cent. sulphuric acid for twenty-four hours. The dark-colored mixture was then poured into 500 cc. of water and heated for five hours on a steam-bath in a flask provided with a condensing tube. The contents of the flask were then neutralized with an excess of calcium carbonate, filtered, and the solution evaporated to about 80 cc.; the liquid was then shaken up with an excess of alcohol and ether to precipitate gummy matters; after standing a short time the clear solution was filtered off and evaporated to 50 cc. A bright straw-colored syrup was obtained, which was set aside in a cool place over sulphuric acid to crystallize.

[1] U. S. Patent 731,290, by Dr. Viggo Drewsen.

[2] Cross and Bevan's "Cellulose," page 82.

Separation and Polarization of d-Glucose from Cane Cellulose.—After standing a few days the syrup began to crystallize and at the end of a week had set to a thick mass of crystals. These were stirred up with alcohol and filtered off on a suction plate. A nearly white product was obtained which, after recrystallization from alcohol, using bone-black, was obtained perfectly pure. After washing with ether, the sugar was dried over sulphuric acid and then at 60° C.; the temperature was finally gradually raised to 90°. In this manner the hydrates of the sugar were broken up without the troublesome melting. 0.2658 gram of the sugar was dissolved to 10 cc. and polarized in a 100 mm. tube. Strong multirotation was observed. The following series of readings was obtained:

Time after solution. Minutes.	Polariscope reading. ° Ventzke.	Specific rotation. $[\alpha]_D^{20°}$
10	+7.5	+97.9
20	6.9	90.0
30	6.1	79.6
60	4.2	54.8
Hours.		
2	4.1	53.5
20	4.05	52.8

The constant specific rotation of *d*-glucose for a 3 per cent. solution, according to the formula of Tollens, $[\alpha]_D = +52.50 + 0.018796\,p + 0.00051683\,p^2$, is +52.6.

To determine whether or not mannose or other sugars beside glucose were present among the hydrolytic products of the cane cellulose, the filtrate from the glucose was treated in the cold with a solution of phenyl hydrazine acetate. No insoluble hydrazones were formed, such as is characteristic of mannose. An examination of the hydrolytic products of the original cane-fiber also failed to indicate other sugars than glucose and the pentoses.

Purification of the Soda Cellulose by Chlorination.—By treatment with chlorine, according to the process of Cross and Bevan, the soda cellulose underwent a loss of 7.7 per cent. in weight and was obtained perfectly white. Microchemical tests failed to indicate the presence of either lignin or pentosans. A distillation with hydrochloric acid gave 4.52 per cent. furfural, which was probably derived entirely from oxycellulose.

CONCLUSION.

Owing to unavoidable mechanical and chemical losses, the results of the foregoing work have more of a qualitative than a quantitative value; an approximation may be made, however, as to the relative yield of the different hydrolytic products. The following results are calculated to 100 parts of pure cane-fiber (protein, ash, fat, etc., excluded):

	Per cent.
Cellulose (including oxycellulose)	55
Xylan	20
Araban	4
Lignin	15
Acetic acid	6

It will be seen that the term pecto-cellulose, which has been applied to sugar-cane fiber, has no chemical value. The term pectose, introduced long ago by Fremy, has been made to cover a large group of unknown cellular substances; now that the composition of the latter is in many cases cleared up, the pecto-celluloses, as a group classification, require a much greater restriction.

The fiber of the sugar-cane resembles very closely in composition the pithy stalks of maize,[1] both being allied to the cereal straws. A distinguishing characteristic of this group is a cellular complex low in cellulose and high in pentosans. This will be made more evident if we compare the sugar-cane with other types.

	Sugar-cane. Per cent.	Oak wood. Per cent.	Hemlock wood. Per cent.
Cellulose	50	55	65
Pentosans (furfuroids)	28	20	7
	78	75	72
Lignin, etc., by difference	22	25	28

The sum of cellulose and pentosans in each case foots up approximately the same, the ratio between the two being complemental. Such a ratio will also be noted in Table II, between the cellulose and pentosans of the different tissues of the cane. These observations are in complete harmony with the theory, that the pentosans may be derived physiologically through modifications of cellulose. Closely related to this formation of pentosans

[1] See work of Tollens and Browne: "Ueber die Bestandtheile des Mais-Marks," *Ber. d. chem. Ges.*, **35**, 1457.

is the formation of the acetic acid group. Cross[1] and Bevan call attention to this fact and point out that the formation of pentosans and acetic acid "increases, *pari passu*, with age, which is in accordance with the view of a common origin." The mechanism of this transformation is not yet fully explained; it seems, however, to be primarily a process of dehydration.

The various substances into which woody fiber may be resolved by hydrolysis have led many to believe that we are dealing with more or less of a mechanical mixture—a substratum of cellulose overlaid with "incrusting substances." This view, however, is no longer tenable. The cellulose, pentosans, lignin and acetic acid obtained from cane-fiber are all hydration products, which, in the parent substances, are intimately combined. While, therefore, a study of the groups split off by hydrolysis is our chiefest aid in investigating the problems of constitution, the mistake must not be committed of regarding the products obtained by chemical treatment as absolutely identical with fiber constituents.

A study of the progressive changes, which the fiber of sugar-cane undergoes during its period of growth, is at present being conducted, and it is hoped that the results of the work will throw additional light upon the theoretical and practical questions involved.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 83.]

OBSERVATIONS ON THE METALLIC ACIDS.[2]

BY ROY D. HALL.

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THE results presented here constitute a very brief chapter in a much larger investigation which has been in progress for some time and which will be published in full in due course. The observations, while preliminary in character, possess distinct value in various lines which the larger research has taken and along which it has been and will continue to be carried in the future.

The starting-out material for the columbic and tantalic oxides was columbite from Haddam, Conn., and from South Dakota.

The Haddam mineral was very iridescent, lamellar and brittle.

[1] Cross and Bevan's "Cellulose," page 192.

[2] From the author's thesis for the Ph.D. degree.

It gave a brown-colored powder, inclined to red. Its specific gravity was found to be 5.75 at 4° C. Upon analysis it showed:

	Per cent.	Per cent.
$Ta_2O_5 + Cb_2O_5$	79.75	79.49
$WO_3 + SnO_2$	0.32	0.32
Fe_2O_3	15.11	15.09
U_3O_8	0.23	0.24
MnO	6.69	5.83

Five kilograms of this substance were reduced to a powder fine enough to pass through a 120-mesh sieve. It was decomposed by the method first suggested by Wolcott Gibbs.[1] The fusions were made fine and treated with two to three times their weight of concentrated sulphuric acid, and heated until the excess of acid had been expelled.

On extracting the mass with boiling water the oxides of columbium and tantalum remained insoluble, with the oxides of silicon, titanium, tungsten, tin and any lead sulphate which had been formed by the action of the acids on the lead vessels. They were washed until the washings no longer gave a precipitate with ammonium hydroxide, and were then covered with a concentrated solution of yellow ammonium sulphide and allowed to stand for several days.

It was supposed that by this treatment all of the tin and tungsten would be removed, while the iron and manganese would be changed to sulphides, which could be dissolved out with dilute sulphuric acid. The residue would then consist only of the oxides of silicon, titanium, columbium and tantalum, and lead sulphate.

Accordingly, the residual oxides were dissolved in hydrofluoric acid and the lead sulphate filtered out. The hydrochloric acid solution was made of such a concentration that on the addition of its equivalent of potassium fluoride most of the tantalum and silicon fluorides separated as double fluorides. These were filtered out and dried. The filtrate was evaporated in large dishes of hard rubber over a water-bath, a slight excess of potassium fluoride being added. When more of the needles of potassium tantalum fluoride separated they were added to the first crop.

The remaining double fluorides were taken out in two fractions, the first consisting largely of potassium columbium oxyfluoride,

[1] *Am. J. Sci.*, **37**, 357 (1864).

while the second contained the same salt, together with the excess of potassium fluoride. The weights of the fractions were:

	Kilos.
$K_2TaF_7 + K_2SiF_6$	1.250
K_2CbOF_5	1.800
$K_2CbOF_5 + KF$	1.325
Total	4.375

After recrystallizing about 100 grams of the middle portion four times, its solution gave a precipitate with hydrogen sulphide, which was found to consist largely of tin sulphide.

A solution of the salt was brought to boiling and saturated with hydrogen sulphide, then filtered and the filtrate tested by diluting and again passing in hydrogen sulphide, with negative results. Upon evaporation of the filtrate to crystallization and analyzing a portion of the crystals obtained, the resulting columbic oxide stained the platinum crucible. Upon taking the crystals up in water and passing in hydrogen sulphide, more tin sulphide was precipitated. It was found impossible to remove all of the tin with hydrogen sulphide even upon crystallizing five times, taking up the crystallizations in water and passing hydrogen sulphide through the solution each time.

The salt remaining after the above treatment was crystallized twice and analyzed.

(1) 0.5508 gram gave 0.2522 gram Cb_2O_5, and 0.3288 gram K_2SO_4, giving an atomic weight of 93.4 for columbium.

(2) 0.5105 gram gave 0.2342 gram Cb_2O_5, and 0.3044 gram K_2SO_4, or an atomic weight of columbium of 93.8.

In both cases the platinum crucible used for the ignition of the oxide was stained.

Most analysts have deemed the mere washing of the oxides of columbium and tantalum with yellow ammonium sulphite sufficient to eliminate the tin and tungsten, but the experience recorded above proves the opposite. Earlier work in this laboratory[1] along this same line demonstrated that prolonged treatment with ammonium sulphide led to the solution of considerable quantities of the oxides of columbium and tantalum, but, despite this fact, it was determined to pursue the last course; consequently, the well-washed oxides from 500 grams of the double fluorides were di-

[1] This Journal, 18, 38.

gested with yellow ammonium sulphide on a water-bath for twenty-four hours, the ammonium sulphide solution decanted, and a fresh portion added. This was repeated four times. The several portions of the ammonium sulphide solutions, when acidified with hydrochloric acid, yielded precipitates, which, filtered, ignited and then reduced in hydrogen, gave more than a gram of metallic tin, the hydrochloric acid solution of which reduced a mercuric chloride solution, gave purple of Cassius with a solution of gold chloride and a brown-black sulphide, soluble in yellow ammonium sulphide.

The part insoluble in hydrochloric acid was ignited, fused with potassium bisulphate and extracted with boiling water. Upon digestion of the hydroxide thus obtained with ammonium hydroxide a large amount dissolved. After filtering, the filtrate gave a precipitate with acids, but was white, not yellow, and did not become yellow after long boiling. There was every evidence that the precipitated tungstic acid contained columbic acid and that, on digesting the mixed hydroxides with ammonium hydroxide, a complex acid had been formed. Long boiling with strong acid was required to precipitate all of the oxide from this solution.

These oxides were filtered out and, after ignition, were fused with sodium carbonate. Upon taking up in water, the sodium carbonate was nearly insoluble in the excess of alkali and could be filtered out. The addition of acid to the filtrate gave a yellow precipitate which answered to all the tests for tungstic oxide.

That part which was insoluble in ammonium hydroxide was also fused with sodium carbonate and likewise found to contain both columbic and tungstic oxides. This would indicate that a separation of the mixed hydroxides of columbium and tungsten by digestion with ammonium hydroxide is impossible.

These experiences, just outlined, confirm the statement of H. Rose, that the oxides of tin and tungsten could not be removed by digestion with ammonium sulphide, so recourse was had to the method adopted by him, namely, fusion with sodium carbonate and sulphur.

The fusions were made in a porcelain crucible at a temperature below that at which sodium carbonate would melt.

Upon extracting with water, the columbic oxide remained in-

soluble as an acid sodium salt; the tin and tungsten going into solution were filtered off.

The acid sodium salt was ignited and changed to the oxide by fusion with potassium bisulphate and extracting with boiling water to remove the sodium and potassium sulphates. A portion of the oxide tested for tin and tungsten by a second fusion with sodium carbonate and sulphur failed to show their presence.

There is no doubt but that one can never be certain of the complete elimination of tin and tungsten from columbium and tantalum oxides unless the last procedure has been scrupulously followed.

The columbic oxide, being thus freed from two of its frequent associates, was changed to potassium columbium oxyfluoride and the latter recrystallized twice, the first portions alone being taken. Each time the dried crystals were taken up in water and boiled a slight residue separated; this was tantalum. In order to remove all of the latter the double fluoride was heated to 150°-175° in an air-bath, when, on dissolving, a considerable residue remained. Upon repeating this twice a tantalum-free preparation was obtained. It weighed about 150 grams.

Another question which constantly obtruded itself was—Is there any titanium in this sample of columbium? Marignac confessed that the columbic oxide used by him was not free from titanium and, further, that he knew of no method by which the latter could be entirely removed. The hydrogen peroxide test for titanic acid was used by Weller in the quantitative estimation of this substance. He employed it to estimate titanium in the presence of zirconium and suggested that it might answer equally well in the presence of columbium, but failed to test the suggestion. Osborne used the method, working in chloride solutions.

As the reaction is not delicate in the presence of fluorides, the solution was changed to chloride in the following way: A portion of the double fluoride was decomposed with sulphuric acid, the oxide well washed, then boiled for a few minutes with concentrated hydrochloric acid, after which it was soluble on diluting or in water. On adding hydrogen peroxide to this solution the color characteristic of titanium appeared.

Another crystallization of the potassium columbium oxyfluoride was made, only the first fraction being taken. It was well washed

and tested for titanium, but showed its presence in amount nearly equal to that in the first sample. The failure to reduce the amount of titanium, shown in successive crystallization, made it evident that this impurity could not be completely eliminated from columbium by a limited number of crystallizations.

The columbium potassium oxyfluoride was next changed to the normal double fluoride and this crystallized in the hope that, not being isomorphous with potassium titanium fluoride, it might separate free from that impurity. Four crystallizations were made from a fairly concentrated hydrofluoric acid solution, when some of the salt was converted into chloride and tested with hydrogen peroxide. Titanium was found, but the amount had decreased by one-half.

The columbium was again changed to oxyfluoride by crystallizing twice from water, the mother-liquors discarded and the crystals dried in an air-bath at 150°. They were analyzed according to the method used by Marignac.

0.5684 gram of salt gave 0.2659 gram of oxide and 0.3485 gram of K_2SO_4, showing an atomic weight for columbium of 92.8.

It seemed advisable now to ascertain the delicacy of the hydrogen peroxide test for titanium, together with the effect of the presence of various substances on its delicacy.

Accordingly, 0.1017 gram of potassium titanium fluoride, containing 0.03356 gram of oxide, was converted into sulphate and made up to 100 cc. One cc. contained 0.00003356 gram TiO_2. One-tenth of this solution or 0.000003356 gram TiO_2 gave the color with hydrogen peroxide when made up to 50 cc. in a Nessler tube of one-inch diameter.

The most dilute standard solution which could well be used for comparison work would be 2 cc. of the above in 50 cc., or 0.00067 gram TiO_2 in 50 cc., each cubic centimeter containing 0.000013 gram TiO_2. With such a solution the successive comparisons against an unknown did not vary over 2 cc., or 0.000026 gram of TiO_2. This agrees fairly well with that found by Weller, who gave the limit of the method as 0.1 mg. in 1 cc.

A solution of potassium titanium fluoride, containing 0.00128 gram of TiO_2, developed a color with hydrogen peroxide equal in intensity to that given by 0.000318 gram in sulphate solution,

or a loss of color due to the presence of fluoride of about three-fourths.

It was observed that the intensity of the color given by hydrogen peroxide with titanium was much lessened by the presence of citric acid, but was not noticeably affected by oxalic or tartaric acid. This behavior, therefore, would permit of the use of the oxalate or binoxalate solution of tantalum and columbium in the making of the tests for titanium, as the moist hydroxides of tantalum and columbium, as well as that of titanium, are readily soluble in potassium binoxalate to stable solutions. When, therefore, 0.5 gram of potassium tantalum fluoride was decomposed by acid, and the hydroxide dissolved in potassium binoxalate, it showed no color with hydrogen peroxide. Upon the addition of 0.00015 gram of TiO_2, a color was produced which was equaled by that of a solution containing 0.000147 gram of titanic oxide, showing that tantalum does not interfere with the color test for titanium in potassium binoxalate solution. The percentage of titanic oxide in the potassium columbium oxyfluoride was determined by destroying the fluoride and dissolving in potassium binoxalate. The tin- and tungsten-free sample, after two crystallizations, showed oxide of titanium to be about 0.5 per cent. of the total oxide; after the four crystallizations from hydrofluoric acid the amount was reduced to 0.25 per cent.

As previously remarked, the question of the complete removal of the last traces of titanium from columbium preparations has long been unanswered.

Krüss and Nilson claimed that by prolonged boiling of the solutions of potassium columbium oxyfluoride, replacing the water lost by evaporation, an insoluble acid salt was produced which contained no titanium. This procedure was adopted, the oxide set free from the salt, dissolved in hydrochloric acid and tested with hydrogen peroxide. 0.032 gram showed the presence of 0.00015 gram of titanum dioxide, or 0.05 per cent., the best that had yet been obtained.

It had been noticed by Smith[1] that sulphur monochloride dissolved the oxides of columbium, tantalum and titanium, in the first two cases forming crystalline bodies and with the oxide of titanium a liquid. It was hoped that by a further study of this

[1] *J. Am. Chem. Soc.*, **20**, 289.

reaction a method might be found which would eliminate the traces of titanium from the columbium.

Oxide of titanium, heated in a sealed tube with sulphur monochloride at 200° for several hours, went into solution, and when the contents of the tube were transferred to a distilling bulb the titanium was volatilized with the sulphur monochloride, probably as the tetrachloride. Oxide of columbium, under the same conditions, went into solution in the sulphur monochloride and separated from it on cooling in transparent yellow prisms, of what was later found to be the pentachloride. On transferring to a distilling bulb the sulphur monochloride could be distilled off and then the columbium chloride distilled over into the stem of the distilling bulb, sealed off and analyzed.

The chloride of columbium came over between 220 and 235°. Prepared in this way, it was difficult to free from sulphur monochloride. After several failures a sample was obtained containing only a small amount of sulphur and analyzing as follows:

0.4400 gram gave 0.2160 gram Cb_2O_5 and 1.1380 grams AgCl, or 0.2815 gram Cl.

0.5395 gram gave 0.2690 gram Cb_2O_5 and 0.0195 gram $BaSO_4$, or 0.0027 gram S.

	Calculated for $CbCl_5$.	Found.	
Cb	34.62	34.7	
Cl	65.38	64.0	
S	....	0.5	
	100.00	99.2	
Cb_2O_5	49.35	49.8	49.1

The analysis was made by decomposing the sample with dilute ammonia water, evaporating to small bulk and filtering off the columbic hydroxide after neutralizing the excess of ammonia with nitric acid. The chlorine was determined in the filtrate. The second sample was decomposed with water and the sulphur oxidized with bromine water, and the filtered hydroxide was washed with dilute ammonium hydroxide to remove all the sulphuric acid. Any oxide of columbium adhering to the glass was dissolved off with potassium binoxalate, or by boiling with concentrated hydrochloric acid and again precipitated by ammonium hydroxide.

In order to see if titanium could be removed from columbium

by means of sulphur monochloride, 1.1 grams of columbic oxide, containing 0.25 per cent. of oxide of titanium, were heated with sulphur monochloride in a sealed tube for fourteen hours.

The contents of the tube were transferred to a distilling bulb and distilled. The sulphur monochloride and the oxide carried with it were decomposed by ammonia water and the ignited oxide tested for titanium. 0.0955 gram obtained was found to contain 0.00066 gram of titanic acid, or 0.7 per cent.

The sublimed crystals of columbic chloride were changed to oxide and 0.4295 gram found to contain 0.00075 gram of TiO_2, or 0.18 per cent., showing only a slight improvement.

The desire to prepare the chloride of columbium free from oxychloride and sulphur monochloride led to an attempt to change the oxide to chloride by heating in a current of sulphur monochloride, and distilling the resulting chloride in a current of chlorine.

Under these conditions the ignited oxide was rapidly changed to chloride at a moderate temperature and with a small amount of sulphur monochloride. Oxychloride was at first formed, but this changed rapidly in the sulphur monochloride vapors to chloride. On cutting out the sulphur monochloride and substituting a current of dry chlorine gas the columbium pentachloride could be distilled and freed from sulphur, as the following analyses show:

(1) 0.6290 gram $CbCl_5$ gave 0.3105 gram Cb_2O_5; 1.6590 grams AgCl, or 0.2178 gram Cb and 0.4101 gram Cl.

(2) 0.4084 gram $CbCl_5$ gave 0.2021 gram Cb_2O_5; 1.0788 grams AgCl, or 0.1418 gram Cb and 0.2658 gram Cl.

	Calculated.	Found. I.	Found. II.
Cl	65.38	65.20	65.33
Cb	34.62	34.63	34.71
	100.00	99.83	100.04
Cb_2O_5	49.35	49.26	49.49

The silver chloride obtained was perfectly white and showed no trace of sulphide.

The chloride of tantalum was prepared in a similar way, because of its higher boiling-point it is easier to free from sulphur monochloride than is columbium chloride.

It was obtained in nearly white crystals, fusing to a light yellow oil. It was analyzed by decomposing in dilute ammonia, allowing to stand twenty-four hours, then adding nitric acid in slight excess, which caused the tantalic hydroxide to separate in flocks and filter readily. The chlorine was determined in the filtrate.

1.4684 grams of $TaCl_5$ gave 0.9085 gram Ta_2O_5; 2.9215 grams AgCl, or 0.7454 gram Ta and 0.7228 gram Cl.

	Calculated.	Found.
Ta	50.76	50.77
Cl	49.24	49.22
	100.00	99.99
Ta_2O_5	61.86	61.87

The ease with which these two difficultly reducible oxides were changed to chlorides in a current of sulphur monochloride vapor led to a series of qualitative experiments to see what oxides could be so changed and if certain quantitative separation might not be effected by the use of sulphur monochloride; also, if various minerals might not be readily decomposed by means of it.

It was found that the oxides of titanium, aluminum, and iron, besides those of columbium and tantalum, were readily changed to volatile chlorides at a moderate temperature.

Oxides of tungsten, vanadium and molybdenum were changed to volatile oxychlorides.

Oxides of zirconium and tin were changed to volatile chlorides, but exposure to a temperature approaching the softening-point of glass for a considerable time was required for complete transformation.

Oxides of boron and silicon were not affected, while chromic oxide was changed to the slightly volatile violet chloride. Oxides of manganese, sodium and those oxides forming non-volatile chlorides were changed to chlorides, the latter remaining in the boat and being soluble in water.

Some of the columbite from the Black Hills, S. D., was readily decomposed, the tantalum, columbium and iron being volatilized and leaving manganese chloride sufficient in weight to give 13 per cent. MnO; that obtained in the analysis was 12.92 per cent.

Chromite was changed to volatile ferric chloride and the violet

chromium chloride, which, calculated to oxide with the gangue, gave 46 per cent. remaining in the boat.

The titanium in rutile was completely expelled and the iron and titanium in ilmenite were driven out, leaving a white residue. All of the titanic oxide was volatilized from a mixture of titanic and silicic acids.

The use of sulphur monochloride affords an excellent and convenient method of preparing the anhydrous chloride of many of the elements. It offers a means of separating those forming volatile chlorides from those forming non-volatile chlorides. It also affords an excellent means of decomposing some of the most refractory minerals.

However, the removal of the titanium had not yet been accomplished. Recalling a statement of Demarçay[1] that columbium is completely precipitated from the solution of its oxyfluoride by exactly neutralizing with ammonium hydroxide and then boiling, while titanium, under similar conditions, was not precipitated, the suggestion was tested.

The hydroxide thus precipitated was dissolved in hydrofluoric acid and the operation repeated.

0.1473 gram of this oxide in hydrochloric acid solution showed no yellow with hydrogen peroxide, while the addition of 0.00003 gram of titanic acid gave the characteristic color for titanium. The amount of titanium present, therefore, was materially less than 0.02 per cent.

When the precipitation was made from a boiling solution, some titanium was brought down with the columbium hydroxide. Four precipitations made in this way, starting with oxyfluoride containing 0.5 per cent. of titanium oxide, gave a product which still had 0.1 per cent. of titanium. Further precipitations in boiling solutions failed to diminish the quantity, while four precipitations in the cold, throwing out each time from one-half to three-fourths of the columbium present, yielded columbic oxide perfectly free from titanium. At least, the most searching tests for it failed to reveal it.

In the course of the present study occasion was taken to make a series of comparative qualitative tests with the double fluorides of titanium, zirconium, columbium and tantalum. The results are exhibited in the appended table.

[1] *Compt. Rend.*, **100**, 740.

Potassium titanium fluoride is much less soluble in a solution containing potassium iodide than in water. The crystals separating from such a solution carry down a large amount of potassium iodide. Thus 1.5 grams of potassium titanium fluoride were dissolved in 37.5 cc. of water, and to this solution were added 112.5 cc. of a cold saturated solution of potassium iodide. The liquid was boiled and became clear. On cooling, a mass of feathery crystals separated. These were freed from mixture by means of a filter-pump, pressed between filter-paper and analyzed.

0.8408 gram of substance gave 0.1273 gram of silver iodide, or 0.0899 gram of potassium iodide, and 0.2320 gram of titanic oxide, or 0.6960 gram of K_2TiF_6.

	Per cent.	
K_2TiF_6	82.8	
KI	10.6	
H_2O	6.6	(by difference)

Potassium bromide showed a similar action. The potassium titanium fluoride which separated carried with it about 10 per cent. of potassium bromide.

These two halides showed a like behavior when their solutions were added to the solution of potassium zirconium fluoride.

The potassium columbium oxyfluoride proved less soluble in solutions of the alkaline halides than in water, while in the solution of potassium tantalum fluoride precipitates were produced by potassium iodide, bromide and chloride.

Solutions of the double fluorides of titanium, zirconium, columbium and tantalum were not affected by potassium bromate, chlorate, perchlorate, dichromate, sodium metaphosphate, sodium pyrophosphate, ammonium sulphate, silver nitrate, mercuric chloride, ammonium oxalate, oxalic, acetic, fumaric, maleic, formic, salicylic, succinic and benzoic acids, α-nitroso-β-naphthol in 50 per cent. acetic acid, sodium molybdate and sodium tungstate.

Reagents.	Titanium. Solution : 5 grams of pure K_2TiF_6 in 400 cc. of water.	Zirconium. Solution : 10 grams of K_2ZrF_6 in 500 cc. of water.	Columbium. Solution : 10 grams of $2KF.CbOF_3$ in 500 cc. of water.	Tantalum. Solution : 1 gram of K_2TaF_7 in 150 cc. of water.
NaOH.	Complete precipitation.	Complete precipitation.	Precipitate, nearly all soluble in slight excess of reagent. Large excess causes separation of crystals of sodium columbate.	Slight permanent precipitate, not soluble in excess. Crystals separate on standing.
$KHCO_3$.	No precipitate in the cold ; incomplete on boiling.	No precipitate.	Precipitate soluble in excess on standing.	
Na_2CO_3.	Precipitation complete.	Precipitation slow, but complete.	Precipitation complete. Nearly all soluble in slight excess. Same as NaOH.	Precipitation after long standing.
$(NH_4)_2CO_3$.	No precipitate in the cold. Slight precipitation after twenty-four hours.	No precipitate.	Precipitate soluble in excess.	Heavy precipitate.
$BaCO_3$ (emulsion).	Precipitation complete in the cold.	Precipitation nearly complete in the cold.	Precipitation nearly complete in the cold after twenty-four hours.	Little reaction in the cold. Precipitation complete on boiling.
KCN.	Precipitation complete.	Precipitat'n complete.	Heavy white precipitate.	Precipitation complete.
KCNS.	A crystalline precipitate on using a concentrated solution of the reagent.	Ditto.	Slight precipitate with concentrated reagent.	Slight precipitate.
$K_4Fe(CN)_6$.		Slight white precipitate.	Yellow precipitate, separating slowly.	A yellow precipitate, forming slowly.
$K_3Fe(CN)_6$.	Crystalline precipitate.	Few granular crystals separated.	No precipitate.	No precipitate.

Reagents.	Titanium. Solution : 5 grams of pure K_2TiF_6 in 400 cc. of water.	Zirconium. Solution : 10 grams of K_2ZrF_6 in 500 cc. of water.	Columbium. Solution : 10 grams of $2KF.CbOF_3$ in 500 cc. of water.	Tantalum. Solution : 1 gram of K_2TaF_7 in 150 cc. of water.
K_2CrO_4.	Almost complete precipitation. Insoluble in water.	White precipitate. Incomplete. Insoluble in water.	Complete precipitation.	Complete precipitation.
KIO_3.	Precipitation complete with an excess of the reagent upon boiling vigorously.	Precipitation complete on boiling.	An equal volume of hot saturated solution of the reagent gave no precipitate. Partial precipitation after long boiling.	No precipitate.
Na_2HPO_4.	Complete precipitation.	Complete precipitat'n.	No precipitation.	No precipitation.
Na_2SO_3.	Precipitate; not complete on boiling. Does not occur in acid solution.	Slow precipitation; almost complete in twenty-four hours.	Complete precipitation in neutral solution.	Precipitation exceedingly slow.
$Na_2S_2O_3$.	Slight precipitate. Forms slowly.	Precipitation slight.		Slight precipitate.
K_2SO_4.	No change.	No change.	No change.	A very heavy precipitate with a cold saturated solution of the reagent. Soluble on warming.
H_2SO_3.	Yellow color.	A light yellow colored precipitate slowly separated.	Slight precipitate after long standing.	Heavy precipitate after standing some time.
$Pb(C_2H_3O_2)_2$.	Heavy precipitate. Soluble in nitric acid.	Heavy precipitate.	Ditto.	Ditto.

Reagents.	Titanium. Solution : 5 grams of pure K_2TiF_6 in 400 cc. of water.	Zirconium. Solution : 10 grams of K_2ZrF_6 in 500 cc. of water.	Columbium. Solution : 10 grams of $2KF.CbOF_3$ in 500 cc. of water.	Tantalum. Solution : 1 gram of K_2TaF_7 in 150 cc. of water.
$BaCl_2$.	Slight precipitate, becoming heavy and flocculent on boiling. Soluble in acids.	Precipitate; soluble in hydrochloric acid.	Slight precipitate after long standing.	Heavy precipitate after standing some time.
Alcohol.	An equal volume of 95 per cent. alcohol precipitated nearly all of the double fluoride.	Crystalline precipitate; soluble on warming.	An equal volume of 95 per cent. gave a heavy gelatinous precipitate.	No precipitate.
$NaC_2H_3O_2$.	Precipitation almost complete on boiling.	Precipitation not complete.	Precipitation complete in the cold.	A heavy white precipitate, nearly complete on boiling.
NH_4—Fumarate.	Precipitation on boiling.	Ditto.	Precipitation complete on boiling.	Precipitation complete on long boiling.
NH_4—Maleate.	Precipitation on boiling.	Ditto.	Ditto.	Ditto.
NH_4—Formate.	Slow precipitation. Nearly complete on boiling.	Incomplete precipitation on boiling.	Precipitation complete on boiling.	Precipitation complete on long boiling.
NH_4—Citrate.	No precipitate; excess of ammonium hydroxide does not cause precipitation.	Ditto.	Ditto.	No precipitate; ammonium hydroxide slowly precipitates on boiling.
Malic acid.	No precipitate, until after the addition of a large excess of ammonium hydroxide.	No precipitation. Subsequent addition of ammonium hydroxide has no effect.	No precipitation. Partial precipitation by an excess of ammonium hydroxide.	No precipitate. Ammonium hydroxide in the cold has no effect, but precipitation occurs on boiling.

Reagents.	Titanium. Solution : 5 grams of pure K_2TiF_6 in 400 cc. of water.	Zirconium. Solution : 10 grams of K_2ZrF_6 in 500 cc. of water.	Columbium. Solution : 10 grams of $2KF.CbOF_3$ in 500 cc. of water.	Tantalum. Solution : 1 gram of K_2TaF_7 in 150 cc. of water.
Na—Benzoate.	Precipitation not complete on boiling.	No precipitation. Subsequent addition of ammonium hydroxide has no effect.	Precipitation complete on boiling.	Slight precipitate.
Tartaric acid.	No precipitate. Prevents precipitation by ammonium hydroxide.	Ditto.	Precipitation in presence of excess of ammonium hydroxide after long boiling.	Slowly precipitated on boiling in the presence of ammonium hydroxide.
Zn + HCl.	Sea-green color.	No color.	Green-brown, passing into deep brown.	No color.
H_2O_2.	Deep yellow color.	No color.	No color.	No color.
Solution of gall nuts.	Neutral solution. No precipitate, red color. Yellow color in presence of a little hydrochloric acid.	Slight white precipitate in acid solution.	No precipitate; reddish color. On the addition of hydrochloric acid and the application of heat the color fades and a brick-red precipitate is produced.	Faint yellow color. Ammonia gives a brown color.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 84.]

THE ELECTROLYTIC DETERMINATION OF NITRIC ACID WITH A ROTATING ANODE.[1]

BY LESLIE HOWARD INGHAM

Received July 26, 1904.

LUCKOW first noted that in the electrolysis of dilute nitric acid no ammonia was produced unless copper sulphate was present, whereas, in the presence of the latter, ammonium sulphate was formed while copper was being plated upon the cathode. Vortmann,[2] in 1890, applied this thought to the quantitative estimation of nitric acid. When all the copper was deposited, the residual liquid was evaporated to a small bulk and, excess of alkali having been added, the ammonia was distilled off into an excess of standard acid and this excess was then titrated back with standard alkali.

Easton, in 1903,[3] studied the procedure of Vortmann and published the conditions which he found to be satisfactory. He distilled off the ammonia and determined it in the usual manner.

The present study of the method was undertaken primarily with a view of ascertaining whether the time of determination could be shortened. Agitation of the electrolyte being known to promote the rapid deposition of metals, it was thought that it might also favor the rapid reduction of nitrates. Another mode of shortening the time would be the omission of the distillation of the ammonia. A suggestion of Vortmann,[2] quoted by Easton, but not used by him, was to acidulate the solution of the nitrate with a known amount of standardized acid and add a solution of copper sulphate containing a definite amount of sulphuric acid. After the reduction of the nitrate this acid would be partly neutralized by the ammonia which had been formed and the excess of acid could be then directly titrated by standard alkali.

This was the course adopted by the writer. The apparatus employed in the reduction was that used in the rapid determination of zinc.

In each experiment the desired quantity of potassium nitrate

[1] From the author's thesis for the Ph.D. degree.

[2] *Ber. d. chem. Ges.*, 1890, p. 2798.

[3] This Journal, **25**, 1042.

was weighed off and dissolved in a small amount of water in a clean platinum dish; the necessary amount of copper sulphate was then pipetted from the stock solution and a measured amount of standard sulphuric acid was added, sufficient to make the electrical resistance low and to insure the solution remaining quite strongly acid during the reduction of the nitrate.

This solution was then diluted to about 125 cc. and electrolyzed with a current of from 4 to 5 amperes and about 10 volts. The exact conditons are stated for each experiment in the tabular exhibit. During the electrolysis the copper was deposited upon the cathode and its equivalent of sulphuric acid was liberated and added to the acid already present, whereby the conductivity was increased and the voltage fell. As the nitric acid was gradually reduced to ammonia the free acid was neutralized and if the current was maintained constant by the rheostat, the voltage gradually rose for about twenty-eight minutes and then became stationary, thereby indicating the end of the reduction. This rise was usually from 5 to 7 volts. The voltages given in the table are those read at the outset of each experiment, to which the above must be added to obtain the final voltage.

The motor having been stopped, the liquid in the dish was siphoned off into a beaker and replaced by distilled water while the current continued; the dish, anode and cover glasses were well washed, the electrical circuit interrupted, and the washings added to the liquid in the beaker. It being unnecessary to weigh the deposited copper, the platinum dish was merely rinsed with nitric acid and washed under the faucet, when it was ready for use again.

The contents of the beaker were rapidly neutralized in the presence of litmus or methyl orange by the standard ammonia solution. The indicators named were found to give identical results. Let it be noted that in the reduction 1 molecule of potassium nitrate gives rise to a molecule of potassium hydroxide and one of ammonia; hence two equivalents of alkali are produced from one equivalent of nitrate, and allowance must be made for this by halving the results obtained by titration. The use of a 0.5-gram sample for analysis just offsets this. The calculation of the standard ammonia solution to its equivalent of N/5 sodium carbonate solution and thence to nitrogen is obvious.

A number of experiments were conducted to ascertain the time.

the amount of copper sulphate, the current strength and speed best suited for the quantitative reduction of nitrates.

(*a*) *Time.*—The first ten experiments were made with reference to the time of reduction. Using 25 cc. of copper sulphate solution, 25 cc. of acid solution and 0.5 gram of nitrate, 5 amperes gave 5.63 per cent., 9.83 per cent., 9.91 per cent. and 11.26 per cent. of nitrogen respectively in ten, fifteen, fifteen and twenty minutes, the theoretical percentage of nitrogen in potassium nitrate being 13.86.

By increasing the time, 4 amperes gave 13.64 per cent. in twenty-five minutes and 13.83 per cent. in thirty minutes.

(*b*) *Amount of Copper Sulphate.*—The above results were obtained with 25 cc. of copper sulphate. Two experiments with 50 cc. gave 8.79 per cent. in twenty minutes and 12.96 per cent. in thirty minutes, showing that the increased amount of copper is not an advantage. Two experiments with but 15 cc. of copper sulphate solution and 30 cc. of standard acid resulted in a reduction of 11.93 per cent. and 13.55 per cent. in twenty and thirty minutes respectively. Increasing the amount of acid to 50 cc. with the same amount of copper gave better results, *viz.*, 13.10 per cent. and 13.83 per cent. in twenty and thirty minutes respectively.

(*c*) *Strength of Current.*—An experiment with 5 amperes gave 13.38 per cent. nitrogen in twenty-five minutes, while 6 amperes gave only 13.19 in twenty minutes. From this it appears that 4 amperes is sufficient current, since that will yield complete reduction in thirty minutes and more current will not do the work in less time.

(*d*) *Speed.*—Two experiments with the speed of rotation of the anode increased to about 560 revolutions per minute gave 12.91 per cent. and 13.19 per cent. in twenty and thirty minutes respectively; the voltage needed was 40, since the contact between the anode and the liquid was poor at this velocity. So much heat was produced that the liquid boiled freely, but no advantage was found in increased speed.

The results and detailed conditions of this work are found in the subjoined table.

Taken.				Conditions.			Calculation.				
Copper sulphate solution. cc.	Potassium nitrate. Gram.	Standard acid. cc.	Copper metal. Gram.	Volts.	Amperes.	Speed.[1]	Time. Minutes.	cc. standard ammonia to titrate.	Ammonia needed equivalent to copper.	Ammonia equivalent to standard acid.	Sum of these, minus ammonia in titration.	Sodium carbonate equivalent to alkali produced in electrolysis.	Percentage of nitrogen found.	Number of experiment.
25	0.5000	25	0.2533	12	5	I	10	44.5	40.0	24.4	19.9	20.1	5.63	1
25	0.5000	25	0.2533	12	5	I	15	29.5	40.0	24.4	34.9	35.1	9.83	2
25	0.5000	25	0.2533	12	5	I	15	29.2	40.0	24.4	35.2	35.4	9.91	3
25	0.5000	25	0.2533	12	5	I	20	24.4	40.0	24.4	40.0	40.2	11.26	4
25	0.5000	25	0.2533	8	3	I	20	32.4	40.0	24.4	32.0	32.2	9.02	5
25	0.5000	25	0.2533	10	4	I	20	15.9	40.0	24.4	48.5	48.7	13.64	6
25	0.5000	25	0.2533	10	4	I	25	15.9	40.0	24.4	48.5	48.7	13.64	7
25	0.5000	25	0.2533	9	4	I	30	15.2	40.0	24.4	49.2	49.4	13.83	8
25	0.5000	25	0.2533	9	4	I	30	15.4	40.0	24.4	49.0	49.2	13.78	9
25	0.5000	25	0.2533	9	4	I	30	15.5	40.0	24.4	48.9	49.1	13.75	10
50	0.5000	25	0.5066	10	4	I	20	73.2	80.0	24.4	31.4	31.4	8.79	11
50	0.5000	25	0.5066	10	4	I	30	58.3	80.0	24.4	46.1	46.3	12.96	12
15	0.5000	30	0.1520	10	4	I	20	10.9	24.0	29.3	42.4	42.6	11.93	13
15	0.5000	30	0.1520	10	4	I	30	5.1	24.0	29.3	48.2	48.4	13.55	14
15	0.5000	50	0.1520	10	4	I	20	26.2	24.0	48.8	46.6	46.8	13.10	15
15	0.5000	50	0.1520	10	4	I	30	23.6	24.0	48.8	49.2	49.4	13.83	16
15	0.5000	50	0.1520	16	6	I	20	25.9	24.0	48.8	46.9	47.1	13.19	17
15	0.5000	50	0.1520	12	5	I	25	25.2	24.0	48.8	47.6	47.8	13.38	18
25	0.5000	25	0.2533	40	4	II	20	18.5	40.0	24.4	45.9	46.1	12.91	19
25	0.5000	25	0.2533	40	4	II	30	17.5	40.0	24.4	46.9	47.1	13.19	20

[1] See thesis.

The above results appear to indicate that the conditions of Experiment 8 are to be preferred. To confirm this a series of ten determinations were made in accordance with those conditions, namely, 25 cc. of copper sulphate solution, representing 0.2533 gram of metallic copper, 25 cc. of the standard sulphuric acid, 0.5 gram of potassium nitrate, 4 amperes, 10 volts at the outset, or 17 volts at the end of reduction, slowest speed and thirty minutes. The dish was not warmed at the outset of the experiment, nor was external heat applied during electrolysis, although the liquid was considerably heated by the current, the final temperature being about 65° C. This continuous series was made in a single afternoon and no results were rejected; consequently they may be taken as representing the probable error of the method.

The following are the percentages of nitrogen found, the theoretical value being 13.86:

Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
13.81	13.79	13.83	13.83	13.94
13.86	13.92	13.92	13.86	13.89

Mean of the series of ten, 13.865.

This method for nitrates compares quite favorably with other methods in point of accuracy. Its advantages in simplicity and speed appear to the writer to be worthy of careful consideration, as a complete determination of the nitric acid content of an alkali nitrate may be made in thirty-five minutes from the time of weighing off the sample.

The applicability of the method to other nitrates than that of potassium will be studied.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 85.]

DETERMINATION AND SEPARATION OF GOLD IN THE ELECTROLYTIC WAY.[1]

BY SARAH P. MILLER.

Received July 26, 1904.

The purpose of this investigation was to ascertain the conditions under which gold could be satisfactorily deposited from its solution:

(*a*) in potassium cyanide;

(*b*) in the presence of phosphoric acid;

[1] From the author's thesis for the Ph.D. degree.

1 See thesis.

(*c*) in sodium sulphide;

and to employ the data thus gathered for its separation from various other metals.

(A) DETERMINATION IN CYANIDE SOLUTION.

To 10 cc. of auric chloride were added 1 gram of potassium cyanide and 150 cc. of water. The precipitated gold was perfectly adherent and was deposited directly upon the sides of the platinum dish in connection with the cathode.

RESULTS.

Gold present. Gram.	Potassium cyanide. Gram.	Dilution. cc.	Current. $N.D_{100}$ =	Volts.	Temperature. °C.	Time. Hour.	Gold found. Gram.
0.1275	1.0	150	0.15–0.20 A	3.0–3.7	65	1	0.1275
0.1275	1.0	150	0.20–0.30 A	3.5–4.0	65	1	0.1277

With the view of separations that might possibly be made, a series of experiments were next carried out, employing the same electrolyte as prevailed in the above determinations, but using a current of low pressure and strength, in order to obtain conditions under which the lowest possible pressure and current strength could be applied and yet completely precipitate the gold from its solution.

The temperature best adapted for the deposition of the metal ranged between 55° C. and 65° C. In the cold the gold was not deposited so rapidly, and, in fact, with the lowest amperage and voltage employed it was not precipitated at all. A temperature above 75° C. also prevented its deposition to some extent.

The results were as follows:

Expt. No.	Gold present. Gram.	Potassium cyanide. Gram.	Dilution. cc.	Current. $N.D_{100}$ =	Volts.	Temperature. °C.	Time. Hours.	Gold found. Gram.
1	0.1291	1.0	150	0.07–0.09 A	1.8–2.0	75	2½	0.1288
2	0.1291	1.0	150	0.04–0.06 A	1.8–2.0	68	2½	0.1293
3	0.1291	1.0	150	0.02–0.15 A	1.8–2.8	60	2	0.1294
4	0.1291	1.0	150	0.03–0.20 A	2.0–3.0	65	2½	0.1290
5	0.1291	1.0	150	0.11–0.04 A	2.5	61	2	0.1291
6	0.1291	1.0	150	0.03–0.02 A	1.8	70	2½	0.1290
7	0.1291	1.0	150	0.04–0.02 A	1.8	65	2½	0.1292

In Experiments 1, 2 and 3, tabulated above, a current of $N.D_{100}$ = 0.015 ampere and 1.6 volts were allowed to act upon the solution for one hour; at the expiration of that time no gold had been precipitated.

It was also found that a current of $N.D_{100}$ = 0.02 ampere and 1.8 volts, although sufficient to give a deposition of gold, failed to bring down the last traces. This was demonstrated by subjecting the solution to those conditions for three hours, and then raising the level of the liquid. After one hour, there being no further precipitation of metal, the liquid was siphoned off, the electrolyte replaced by water, the current interrupted and the deposit weighed after washing with hot water, alcohol and ether and drying in a desiccator. Instead of 0.1291 gram of gold present there was obtained (*a*) 0.1260 gram and (*b*) 0.1259 gram of metal.

As shown, however, in Experiments 6 and 7, a current of 1.8 volts with 0.02-0.04 ampere for one and one-half hours, then increased so as to maintain a voltage of 1.8, allows of the complete precipitation of the gold.

The method of treating the deposits of metal, as outlined above, was adhered to in all experiments, unless otherwise stated. And in all cases (unless special treatment is cited) the gold was deposited directly upon the platinum, and after weighing dissolved off by introducing very dilute potassium cyanide (0.5 gram in 150 cc. of water) into the dish, and connecting the latter with the anode of a battery yielding a very feeble current (0.2 ampere and 5 volts), using a copper wire in connection with the cathode.

RATE OF PRECIPITATION OF GOLD FROM DOUBLE CYANIDE SOLUTION.

In a series of experiments made to determine the rate of precipitation of gold from its double cyanide, a solution containing 0.1236 gram of gold, 1 gram of potassium cyanide and diluted to 125 cc. was acted upon by a current of $N.D_{100}$ = 0.03 ampere and 2.5 volts. The electrolyte was warmed to 50° C. before subjecting it to the current.

After fifteen minutes there was no deposit of gold.

After thirty minutes the deposit of gold weighed 0.0006 gram.

After forty-five minutes the deposit of gold weighed 0.0030 gram.

After sixty minutes the deposit of gold weighed 0.0051 gram.

After seventy-five minutes the deposit of gold weighed 0.0083 gram.

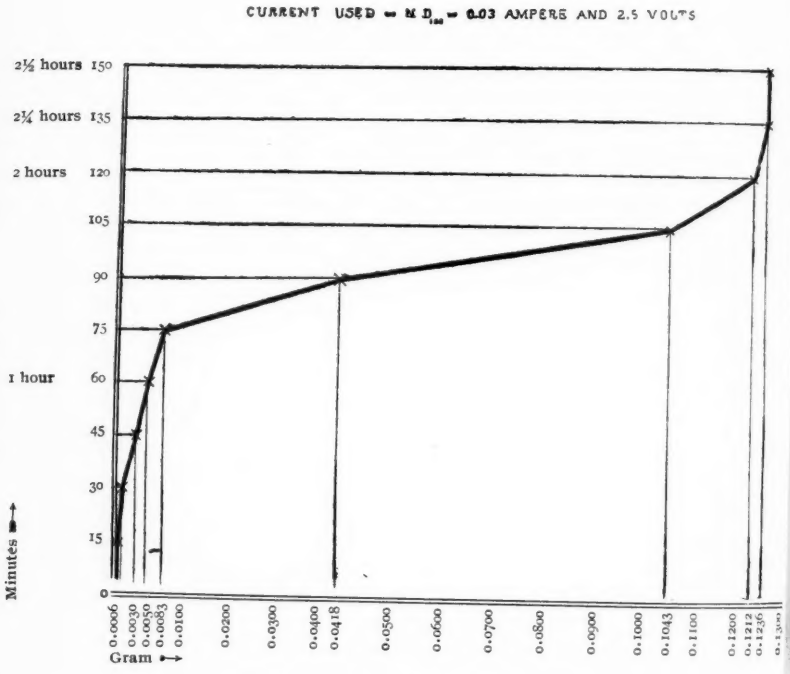
After ninety minutes the deposit of gold weighed 0.0418 gram.

After one hundred and five minutes the deposit of gold weighed 0.1047 gram.

After one hundred and thirty-five minutes the deposit of gold weighed 0.1236 gram.

After one hundred and fifty minutes the deposit of gold weighed 0.1236 gram.

CURVE SHOWING THE RATE OF PRECIPITATION OF GOLD FROM DOUBLE CYANIDE SOLUTION.



SEPARATIONS IN CYANIDE SOLUTION.

Among the metals, not as yet successfully separated from gold, may be mentioned, iron, cadmium, silver, lead and mercury.

Gold from Iron.

Ferrous ammonium sulphate was taken in sufficient quantity to yield 0.1300 gram of metallic iron, and dissolved in 10 cc. of water, filtered immediately into 3 grams of potassium cyanide, warmed and quickly filtered—this procedure insured the presence of all of the iron in the ferrous state. To this dark brown solution were added 10 cc. of auric chloride, containing 0.1286 gram of metallic gold, and the whole diluted to 125 cc.

RESULTS.

Expt. No.	Gold present.	Iron present.	Potassium cyanide.	Dilution.	Current.	Volts.	Temperature.	Time.	Gold found.
	Gram.	Gram.	Gram.	cc.	$N.D_{100}$ =		° C.	Hours.	Gram.
1	0.1286	0.1300	3.0	125	0.13–0.36 A	2.3–3.0	65	2½	0.1284
2	0.1286	0.1300	3.0	125	0.06–0.11 A	2.3–3.0	Cold	Night	0.1285
3	0.1286	0.1300	3.0	125	0.17–0.30 A	2.5–3.0	64	3	0.1285
4	0.1286	0.1300	3.0	125	0.11–0.12 A	2.2–3.0	Cold	Night	0.1284

By several experiments it was demonstrated that a current of $N.D_{100} = 0.05$-0.11 ampere and 1.7-2.3 volts; other conditions, as previously given, failed to completely precipitate the gold, 0.1261 gram being found and 0.1286 gram being present.

In all four experiments cited above, the gold was completely precipitated from the solutions, and was free from iron.

Gold from Cadmium.

The separation of these metals in an alkaline cyanide electrolyte has never been recorded. A series of experiments with the most varying conditions was instituted, but resulted negatively. The accompanying diagrams express plainly the facts obtained in the many trials which were conducted.

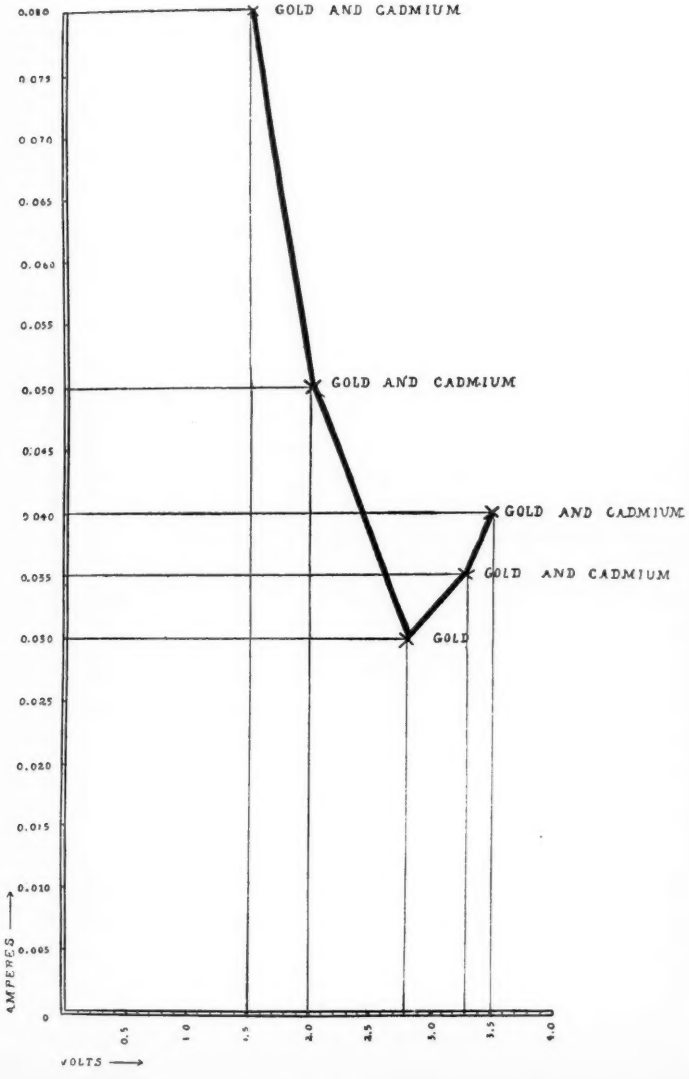
Gold from Silver.

A silver nitrate solution containing 0.1195 gram of silver to which had been added 1 gram of potassium cyanide and 2 grams of potassium hydroxide diluted to 125 cc. was subjected to the current.

An auric chloride solution containing 0.1667 gram of gold and 1 gram of potassium cyanide and 2 grams of potassium hydroxide, 125 cc. dilution, was similarly treated.

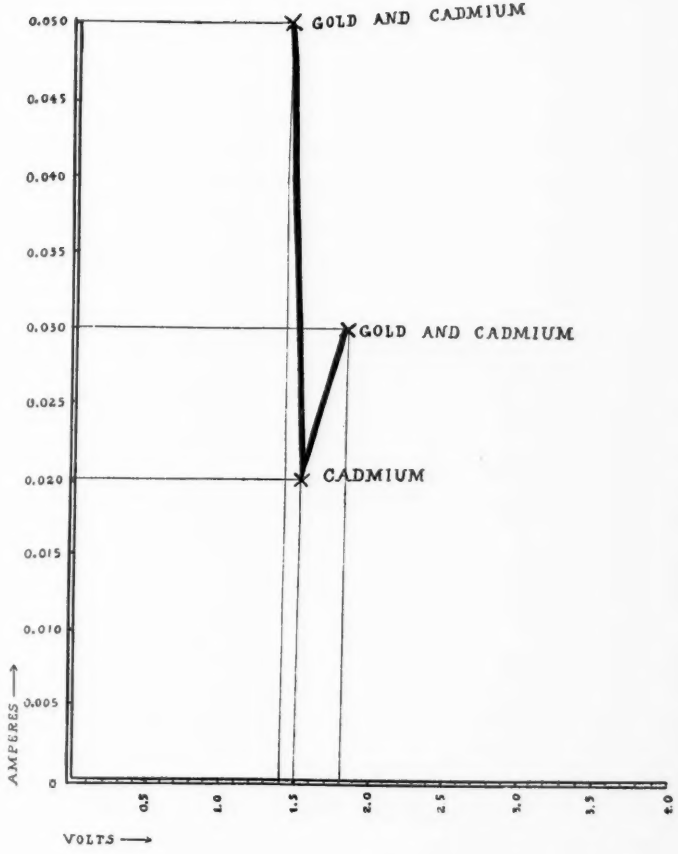
I.

HEATED TO 70° C



II.

IN THE COLD



Silver alone (0.1195 gram).	Gold alone (0.1667 gram).
Over night (cold).	Over night (cold).
$N.D_{100}$ = 0.009 to 0.015 ampere, and 1.6 to 1.8 volts = 0.1190 gram of silver found.	$N.D_{100}$ = 0.01 ampere, and 1.6 volts = no deposit.
Heated to 45° to 50° C.	Heated to 45° to 50° C.
$N.D_{100}$ = 0.01 to 0.02 ampere, and 1.5 to 1.75 volts = 0.1191 gram of silver found.	$N.D_{100}$ = 0.015 ampere and 1.6 volts = no deposit.

With a current of $N.D_{100}$ = 0.025 to 0.03 ampere and 2 to 2.5 volts, 0.1579 gram of gold was deposited.

With these facts as a basis, the separation of silver from gold was tried.

The problem resolved itself into the effort to obtain, as far as possible, a high current strength with a very low pressure. In order to obtain such a relation between current strength and pressure the electrodes were varied in these respects—as to their size relation and their distance apart, the electrolyte being changed in regard to proportions of potassium cyanide and caustic potash present.

The auric chloride used contained 0.1200 gram of metallic gold in 10 cc.; 2 grams of potassium cyanide; the silver nitrate, containing 0.1199 gram of silver; 2 grams of caustic potash; and this solution was diluted to 125 cc.

Experiment 1.—At 5 o'clock in the evening the above solution was subjected to the action of the current—$N.D_{100}$ = 0.02 ampere and 1.5 volts. A perfectly white deposit began to appear almost immediately. The following morning the current registered 0.01 ampere and 1.4 volts—and there was no indication of any metal on the platinum dish serving as cathode.

Experiment 2.—The electrolyte was the same as in Experiment 1. The temperature of 45° C. was maintained. The current $N.D_{100}$ = 0.02 ampere and 1.45 volts at first caused precipitation of metal. After fifteen minutes the current fell to 0.015 ampere and 1.3 volts, and the deposit which had formed was redissolved. The current was raised to 0.025 ampere and 1.5 volts and deposition of metal began. After two hours the level of the liquid was raised. There seemed to be no further deposition of metal; on raising the current to 0.03 ampere and 1.8 volts, however, more metal was precipitated. In one-half hour the current was inter-

rupted (after first siphoning off the electrolyte and replacing it with water) and the usual procedure of treating the deposit carried out—when the deposit appeared uniformly light yellow in color. It weighed 0.1973 gram, the liquid was free from silver, hence 0.0774 gram approximately of gold had also been deposited.

Experiment 3.—The electrolyte was the same as was used in the two preceding experiments. The current was held at 0.015 ampere and 1.6 volts for two hours, when the deposit, after washing with warm water, alcohol and ether, and drying, was weighed. There had been precipitated 0.0935 gram of metallic silver (= 77 per cent. of silver present) absolutely free from gold.

Experiment 4.—The deposit which was obtained weighed 0.2003 gram and had a pale yellow color. The current at first was $N.D_{100} = 0.02$ ampere and 1.4 volts. After two hours this was increased to 0.025 ampere and 1.7 volts, and kept there for one-half hour. There was no indication of silver in the solution, so apparently 0.0804 gram of gold had also been deposited.

In another experiment with the final results similar to those of Experiments 2 and 4, the varying effects of temperature were demonstrated. In the cold a deposition of silver began with a current of 0.015 ampere and 1.45 volts. A uniform coating, white in appearance, covered the dish. One hour later this had entirely disappeared. Heat was applied when the deposit again appeared. In a short time it again disappeared, the temperature registering at this time 78° C. On cooling the solution the coating again appeared and remained with a temperature ranging from 45° to 55° C.

With all of the preceding trials a platinum dish of 175 cc. capacity was used as cathode, and a large platinum spiral of 7 cm. diameter as anode.

Varying amounts of potassium cyanide and caustic potash were tried: One gram of potassium cyanide; 2 grams of caustic potash; 3 grams of potassium cyanide; 2 grams of caustic potash; and 4 grams of potassium cyanide; 2 grams of caustic potash.

The results were the same in all cases; there was no separation. If a low enough current was used to yield silver free from gold, more than 80 per cent. of the silver was never deposited from its solution. When a current of sufficient strength to precipitate the

last traces of silver was employed, varying amounts of gold were carried down with the silver.

Changes in the electrodes, and with each of these changes variations in the proportion of potassium cyanide to potassium hydroxide, were next tried, as follows:

A platinum dish of 175 cc. capacity was made the anode, a platinum gauze (5 x 10 cm.) the cathode. In other experiments the platinum gauze served as the anode and the dish as the cathode.

Two plates of platinum (5 x 10 cm.) were used: The one, in connection with the anode, was rolled and fastened with platinum wire; the other surrounded it, being equally distant from it at all points; a beaker held the solution into which the electrodes were introduced.

When all of the silver was precipitated, gold was invariably present. In some cases the deposit was perfectly white in color, but when treated with nitric acid, the silver would be shown to have been covering a layer of gold. Oftener, however, the deposit was of a very pale yellow color, when in response to treatment with nitric acid the gold would be seen as a thin film covering the silver. In a few cases it seemed probable that the two metals had been simultaneously precipitated and were in consequence intimately combined in the deposit.

The expedient of first coating the platinum used in connection with the cathode received attention; also varying the electrolyte as to relative amounts of cyanide and caustic potash present, and varying the electrodes as described above, but with no better results.

No success was attained in the attempts to separate gold from mercury in a cyanide solution, or in solutions containing both an alkaline cyanide and an alkaline hydroxide.

(B) DETERMINATION IN PHOSPHATE SOLUTION.

A solution containing 10 cc. of auric chloride (= 0.1286 gram metallic gold), 20 cc. of disodium hydrogen phosphate (sp. gr. 1.028) and 5 cc. of phosphoric acid (sp. gr. 1.35) was diluted to 125 cc., warmed to 65° C. before allowing the current to pass through; and electrolyzed with a current of $N.D_{100} = 0.07$ ampere and 1 to 2 volts. After one and one-half hours the level of the liquid was raised and the current increased to $N.D_{100} = 0.12$ ampere and 2.5 volts. There was no further deposition of metal.

The deposit was brown, and in washing with alcohol and ether some of it was detached. The current used had evidently been too strong.

Other experiments followed, using a lower current; in these the deposits, although more compact and adherent, warm water only being used for washing, were not of bright yellow color. Dark specks appeared on the deposits. In weighing them they were all found to be nearly 0.0008 gram too heavy.

The test made for phosphorus in the deposited gold failed to reveal its presence.

A solution of disodium hydrogen phosphate and free phosphoric acid was electrolyzed, but gave no deposit.

Gently igniting the dish containing the deposit, by passing it several times over a small flame of a Bunsen burner, gave a bright yellow deposit of gold.

A deposit weighing 0.0858 gram was thus treated and weighed 0.0847 gram after the first heating, 0.0846 gram after the second heating, and 0.0846 gram after the third heating. There was present 0.0849 gram of gold.

The gentle ignition, as observed from the three weighings, was not sufficient to volatilize any of the gold. The excess of weight of the deposit was probaby due to traces of organic matter in the disodium hydrogen phosphate or in the phosphoric acid.

RESULTS.

Expt. No.	Gold present.	Disodium hydrogen phosphate (sp. gr. 1.028).	Phosphoric acid (sp. gr. 1.35).	Dilution.	Time.	Temperature.	Current.	Volts.	Gold found before ignit'n.	Gold found after ignition.
	Gram.	cc.	cc.	cc.	Hrs.	° C.	$N.D_{100}$ =		Gram.	Gram.
1	0.0849	20	5	125	2	60	0.02–0.015 A	1.0–1.8	0.0855	0.0847
2	0.0849	20	5	125	2	67	0.02 A	1.0–2.0	0.0857	0.0848
3	0.1196	20	5	125	3	60	0.03 A	1.0–2.0	0.1204	0.1197
4	0.1188	20	5	125	2	64	0.02–0.04 A	1.6–2.0	0.1196	0.1187
5	0.1188	20	5	125	2	60	0.02–0.03 A	1.0–2.0	0.1192	0.1185

In all of these precipitations the deposits were perfectly adherent and free from phosphorus, and after heating were of a bright yellow color.

SEPARATIONS IN PHOSPHATE SOLUTION.

Gold from Cadmium.

Cadmium sulphate containing 0.1107 gram of cadmium was

used. In every case the solution was previously heated to 50°-60° C. before allowing the current to act upon the solution. Disodium hydrogen phosphate (sp. gr. 1.028) and phosphoric acid (sp. gr. 1.35) were used in amounts of 40 cc. of the former and 10 cc. of the free acid; 30 cc. of the first and 8 cc. of free phosphoric acid; and 20 cc. of disodium phosphate and 5 cc. of free phosphoric acid. The results seemed to be equally satisfactory; 20 cc. of disodium hydrogen phosphate and 5 cc. of phosphoric acid were most frequently used.

No cadmium or phosphorus was found in the precipitated gold, the deposits were perfectly compact and, after heating, bright in appearance. Warm water only was used in washing the gold precipitated from phosphate solution.

RESULTS.

Gold present. Gram.	Cadmium present. Gram.	Dilution. cc.	Temperature. ° C.	Time. Hrs.	Current. $N.D_{100}$ =	Volts.	Gold found after heating. Gram.
0.1188	0.1107	125	60	4	0.02–0.03 A	1.0–2.2	0.1190
0.1696	0.1107	125	65	4½	0.02 A	1.0–1.7	0.1697
0.1188	0.1107	125	55	5	0.02 A	1.1–2.0	0.1187
0.1448	0.1107	125	66	5	0.03 A	1.0–2.0	0.1450
0.1448	0.1107	125	66	4	0.02 A	1.0–1.8	0.1447

Gold from Iron.

Ferric ammonium sulphate was the salt used, containing 0.1100 gram of iron in 10 cc. Total dilution equaled 125 cc. The temperature was 52° C. Forty cc. of disodium hydrogen phosphate (sp. gr. 1.028), 10 cc. of free phosphoric acid (sp. gr. 1.35) and 0.1188 gram of gold were present.

The current acting upon the solution with a strength of $N.D_{100}$ = 0.03 to 0.06 ampere and 1.2 to 2 volts failed to precipitate the last traces of gold: (1) Gold found, 0.1163 gram; gold present, 0.1188 gram. (2) Gold found, 0.1168 gram; gold present, 0.1188 gram. (3) Gold found, 0.1155 gram; gold present, 0.1188 gram.

The solution was made more dilute, and the current increased, especially for the last half-hour. The results were then more satisfactory.

Expt. No.	Gold present. Gram.	Iron present. Gram.	Dilution. cc.	Time. Hours.	Temperature. ° C.	Current. $N.D_{100}$ =	Volts.	Gold found after ignition. Gram.
1	0.1188	0.1100	150	6	63	0.02–0.16 A	1.0–3.6	0.1182
2	0.1188	0.1100	150	6	67	0.02–0.17 A	1.0–3.0	0.1190
3	0.1188	0.1100	150	5	62	0.02–0.08 A	1.0–2.7	0.1189
4	0.1188	0.1100	150	5	62	0.02–0.08 A	1.0–2.7	0.1189
5	0.1188	0.1100	150	5	62	0.02–0.08 A	1.0–2.5	0.1187
6	0.1188	0.1100	150	5	63	0.02–0.10 A	1.0–2.7	0.1185

In Experiments 1 and 2 the gold was not perfectly adherent. The current strength was lowered and in Experiments 3, 4 and 5 the deposit was perfectly adherent, of a bright yellow color after heating, and was free from iron and phosphorus.

Gold from Zinc.

Zinc sulphate (= 0.1150 gram of zinc) and 10 cc. of auric chloride, 30 cc. of disodium hydrogen phosphate (sp. gr. 1.028), and 6 cc. of phosphoric acid (sp. gr. 1.35) were diluted to 150 cc. and electrolyzed.

RESULTS.

Gold present. Gram.	Zinc present. Gram.	Time. Hours.	Temperature. °C.	Current. $N.D_{100}$ =	Volts.	Gold found after heating. Gram.
0.1148	0.1150	3½	66	0.03 A	1.8–2.0	0.1151
0.1148	0.1150	3	61	0.03–0.04 A	1.0–2.0	0.1145
0.1117	0.1150	2	69	0.03–0.05 A	2.0–2.5	0.1113
0.1117	0.1150	2	69	0.03–0.05 A	2.0–2.5	0.1114
0.1117	0.1150	2	67	0.04 A	2.0–2.5	0.1115

Zinc was not found in the precipitated metal.

Gold from Cobalt.

It was discovered, after repeated experiments, that the separation was effected more satisfactorily in rather dilute solutions. Accordingly, a solution of auric chloride, 30 cc. of disodium hydrogen phosphate (sp. gr. 1.028), 6 cc. of phosphoric acid (sp. gr. 1.35) and cobalt nitrate, containing 0.1200 gram of cobalt, was diluted to 150 cc. to 200 cc. and electrolyzed.

RESULTS.

Gold present. Gram.	Cobalt present. Gram.	Time. Hours.	Temperature. °C.	Current. $N.D_{100}$ =	Volts.	Gold found after heating. Gram.
0.1219	0.1200	2½	53	0.03–0.04 A	1.2–2.0	0.1216
0.1219	0.1200	4	55	0.04 A	1.2–2.3	0.1214
0.1219	0.1200	3	60	0.03–0.04 A	1.1–2.0	0.1217
0.1237	0.1200	2½	78	0.03 A	0.8–1.8	0.1235
0.1237	0.1200	3	58	0.04–0.08 A	1.1–2.2	0.1238
0.1237	0.1200	2	66	0.04 A	1.1–2.0	0.1236
0.1237	0.1200	2	62	0.03–0.06 A	1.1–2.0	0.1239
0.1237	0.1200	2	58	0.03–0.05 A	1.1–2.0	0.1235

Cobalt was not precipitated.

Gold from Nickel.

A solution of 150 cc. volume containing 0.1200 gram of nickel

as nitrate, 40 cc. of disodium hydrogen phosphate (sp. gr. 1.028), 6 cc. of phosphoric acid (sp. gr. 1.35) and 10 cc. of auric chloride, containing 0.1236 gram of gold, was electrolyzed with the following results:

Gold present. Gram.	Nickel present. Gram.	Temperature. °C.	Time. Hours.	Dilution. cc.	Current. $N.D_{100}$ =	Volts.	Gold found after heating. Gram.
0.1236	0.1200	55	4	150	0.04–0.07 A	0.8–2.4	0.1232
0.1236	0.1200	68	4	150	0.04–0.06 A	1.0–2.2	0.1236
0.1236	0.1200	62	3	175	0.03–0.06 A	1.0–2.0	0.1239
0.1236	0.1200	60	2	175	0.03–0.06 A	1.0–2.0	0.1233

The gold deposited showed no trace of nickel.

Gold from Copper.

The electrolyte consisted of copper sulphate (= 0.1200 gram of copper), 40 cc. of disodium hydrogen phosphate (sp. gr. 1.028), 10 cc. of phosphoric acid (sp gr. 1.35) and 10 cc. of auric chloride (= 0.1188 gram of gold). Dilution, 125 cc.

A current of $N.D_{100} = 0.03$ ampere and 2 volts acted on the above solution in the cold through the night. The deposit weighed 0.2047 gram, 0.1188 gram of gold being present. Copper was present with the gold.

In a second trial, using the same electrolyte as above, but a current of $N.D_{100} = 0.02$ ampere and 1 volt, with a temperature of 54° C., after three hours the deposit weighed 0.1112 gram of gold free from copper, 0.1188 gram of gold being present. This same current, however, failed to bring down the last traces of the gold from its solution.

In all precipitations of gold from acid phosphate solution a platinum dish of 175 cc. to 200 cc. capacity was used in connection with the cathode, a platinum spiral with the anode. The depositions were washed only with cold and warm distilled water after siphoning off the liquid and replacing it with water. They were also heated gently either by passing the dish several times over a small flame of a Bunsen burner or by placing the dish on a warm iron plate.

(c) DETERMINATION IN SODIUM SULPHIDE SOLUTION.

A solution of 150 cc., in which were 0.1276 gram of gold, and 15 cc. of sodium sulphide (sp. gr. 1.19), heated to 61° C., was electrolyzed with a current of 0.1 ampere and 0.1 to 0.2 ampere, and

2.4 to 3 volts. In two hours there was deposited (1) 0.1272 gram, and (2) 0.1277 gram of gold.

To the auric chloride were added 50 cc. of water, then the sodium sulphide and the solution warmed carefully until it became clear, and finally diluted to 150 cc. and electrolyzed. The deposited gold was perfectly adherent, and of a shining yellow color, appearing like polished metal.

The separation of gold from arsenic, molybdenum and tungsten may be effected by observing the conditions given for the determination of gold from its sodium sulphide solution.

Separations of gold from mercury and tin were not effected.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 86.]

THE USE OF A ROTATING ANODE IN THE ELECTROLYTIC ESTIMATION OF ZINC.[1]

BY LESLIE HOWARD INGHAM.

Received July 26, 1904.

THE purpose of the present investigation was to ascertain how rapidly the metal zinc could be electrolytically precipitated with the aid of a rotating anode.

The electrolytes employed were solutions of zinc in the presence of sodium hydroxide, sodium acetate, sodium formate and potassium cyanide.

The rate of precipitation of zinc from each of the electrolytes was also studied, after which experiments were instituted to discover how quickly the content of metal in zinc blende could be estimated. It is believed that these experiments indicate which electrolyte is preferable in each case, and demonstrate conclusively that the electrolytic procedure for the estimation of zinc is preferable to the ordinary gravimetric or volumetric methods.

The Apparatus.—The depositions were made upon platinum dishes of the usual form. The anode was a platinum wire 1 mm. in diameter, bent into a spiral 2 inches in diameter. The plane

[1] From the author's thesis presented to the University of Pennsylvania for the Ph.D. degree.

of the spiral was nearly flat, but slightly depressed in the center in dish-form to conform approximately to the figure which the surface of the liquid assumes in the dish while agitated.

The anode was rotated by a small electric motor made by the Elektrochemische Werkstätte in Darmstadt, which received its current from the 110-volt lightning circuit by means of the usual drop-cord and plug. The motor rotated at about 1500 turns per minute and was provided with a three-step cone-pulley. A corresponding three-step pulley on the vertical shaft, which carried the anode, permitted the latter to be rotated at three different speeds approximating 230, 560 and 1750 revolutions per minute. The belt was usually run on the smallest pulley of the armature and the largest of the shaft, thus giving the anode the slowest speed. This speed is designated as I, the faster speeds being II and III. The latter was never used in the precipitation of zinc.

The amount of liquid in the dish was usually about 125 cc. As the agitation of the electrolyte caused the level of the liquid to rise at the walls of the dish, the amount of cathode surface exposed varied constantly. The figures given for current strength will, in every case, be those read directly from the ammeter, but since the cathode surface was kept as near 100 sq. cm. as was possible under the circumstances, these amperages may be considered as equivalent to those implied in the expression $N.D_{100} =$ ampere.

(A) SODIUM ACETATE ELECTROLYTE.

The conditions for the precipitation of zinc from an acetate electrolyte, as given by Exner,[1] were conformed to in the following experiments: The platinum dishes were first coated electrolytically with silver and this deposit washed with water and alcohol, ignited and weighed. The zinc solution was then pipetted into the dish, the desired reagents added and the solution heated nearly to boiling while being held over a free flame in nickel forceps. Heat was not applied during electrolysis, as the electrical energy expended was sufficient to keep the liquid near its boiling-point.

The lack of agreement between the theoretical and required amount of zinc was not thought remarkable, since the specimen of zinc sulphate used was poorly crystallized and appeared to have been formed from a hot supersaturated solution.

[1] This Journal, **25**, 896.

The following results were obtained:

Zn. taken. Gram.	$NaC_2H_3O_2$. Grams.	$HC_2H_3O_2$ (30 per ct.). Drops.	Amperes.	Volts.	Time. Minutes.	Speed.	Zn. found. Gram.	Expt. No.
0.2503	3	4	4	12	10	I	0.2615	1
0.2503	3	4	4	14	10	II	0.2614	2
0.2503	3	4	4	14	10	II	0.2617	3
0.2503	3	4	4	14	10	II	0.2619	4
0.2503	3	6	4	17	15	II	0.2624	5
0.5005	3	6	4	12	15	I	0.5210	6
0.5005	3	4	4	13	15	I	0.5217	7
0.5005	3	6	4	12	15	I	0.5191	8
0.5005	3	6	4	12	15	I	0.5210	9
0.5005	3	6	4	17	15	I	0.5221	10
0.5005	3	6	4	17	15	II	0.5204	11
0.5005	3	6	4	17	15	II	0.5204	12
0.3504	3	6	4	11	15	I	0.3662	13
0.3504	3	6	4	11	15	I	0.3665	14
0.3504	3	6	4	11	15	I	0.3660	15
0.3504	3	6	4	11	15	I	0.3658	16

After the deposit was weighed the zinc and silver were removed together by heating gently with nitric acid (sp. gr. 1.2). The gray deposit dissolved very readily, leaving the platinum dish clean and bright. This was then resilvered and weighed as described above. This mode of cleaning the silver and zinc from the dish was subsequently found to be unnecessary, however, as a dilute solution of sulphuric acid will remove the zinc and leave the silver practically unattacked. Although this was not discovered until later, it will be convenient to describe here the manipulation which was finally adopted. After the dish with its deposit was weighed it was filled to the brim with sulphuric acid previously diluted with about fifty times its volume of water; the dish was then set aside until visible action ceased. The solution was then poured into a beaker and the dish rinsed with water and heated to a faint redness over a free flame while held in nickel forceps. It was then cooled under the faucet and filled a second time with the dilute acid, rinsed after a few moments, heated as before and given a third treatment with the same acid. After the weak acid had been poured away the dish was given a final rinsing in clean water, wiped dry externally and ignited, cooled in a desiccator and weighed. By this treatment the dish lost only about

0.5 mg. of silver each time it was used and one coat of silver sufficed for over a hundred determinations of zinc. The entire time spent in cleaning the dish need not exceed six minutes. Some annoyance was experienced at the outset in the form of high results and a brown anodic stain, which was found to be due to lead acetate in the sodium acetate, and entirely disappeared upon the removal of the lead. All the deposits from a sodium acetate electrolyte consisted of exceedingly minute flat crystals, gray in color and very adherent.

(B) SODIUM HYDROXIDE ELECTROLYTE.

The conditions given by Exner for the deposition of zinc from a solution of sodium zincate in the presence of a large excess of alkali were verified in the following experiments:

For each experiment 25 cc. of solution (= 0.2490 gram of zinc) were taken, together with the stated amount of sodium hydroxide in stick form. After all was dissolved the liquid was washed into a platinum dish which had been previously coated with silver and weighed, diluted to about 125 cc., then electrolyzed with the current and pressure given in the tabular exhibit below. At the expiration of the stated time the liquid in the dish was siphoned off and replaced by cold water and the circuit interrupted. The following are among the results obtained:

Zinc taken. Gram.	NaOH. Grams.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.	No.	K_2SO_4. Gram.
0.2490	8	5	5	15	0.2481	1	0.0
0.2490	8	5	5	15	0.2476	2	0.0
0.2490	8	5	5	20	0.2492	3	0.0
0.2490	8	5	6	15	0.2489	4	0.0
0.2490	8	5	6	15	0.2487	5	0.0
0.2490	8	5	6	15	0.2492	6	0.0
0.2490	8	5	6	15	0.2492	7	0.0
0.2490	8	5	6	15	0.2489	8	equivalent
0.2490	8	5	6	15	0.2488	9	"
0.2490	8	5	6	15	0.2494	10	"
0.2490	8	5	6	15	0.2492	11	"

In Experiments 8 to 11 sufficient potassium sulphate was added to form an equivalent with the zinc sulphate in the proportion $ZnSO_4.K_2SO_4$. This addition presents no advantage.

Blank experiments made with sodium hydroxide solution yielded 0.0000 and 0.0001 gram. The deposits of zinc obtained from

the sodium hydroxide solution were very adherent, smooth, hard, gray in color, and so homogeneous that crystalline structure could not be detected by the unaided eye.

Experiments were conducted to ascertain the amount of sodium hydroxide needed for the best results. In each experiment 25 cc. of the zinc solution were used; to precipitate and redissolve the metal present required about 1 gram of sodium hydroxide, but more should be employed in order to increase the conductivity of the solution.

The results were as follows:

Zinc taken. Gram.	NaOH. Grams.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.	No.
0.2490	2	5	10	20	0.2490	1
0.2490	3	5	8½	20	0.2489	2
0.2490	3	5	8½	20	0.2490	3
0.2490	4	5	6	20	0.2485	4
0.2490	4	5	6	20	0.2489	5
0.2490	5	5	5	20	0.2489	6
0.2490	5	5	5	20	0.2489	7
0.2490	6	5	5	20	0.2489	8
0.2490	6	5	5	20	0.2489	9
0.2490	7	5	5	20	0.2490	10
0.2490	7	5	5	20	0.2490	11
0.2490	10	5	5	20	0.2493	12
0.2490	12	5	4½	20	0.2490	13
0.2490	6	10	8	10	0.2472	14
0.2490	6	5	5	10	0.2480	15

It appears that the amount of sodium hydroxide used may vary within quite wide limits. The last two observations show that the time cannot well be reduced as low as ten minutes even by the use of a current as great as 10 amperes. Portions of the same zinc salt solution were also electrolyzed in the presence of sodium acetate, employing the conditions mentioned under that electrolyte in (A). The results were 0.2488 gram, 0.2491 gram, 0.2487 gram, 0.2486 gram, 0.2490 gram, agreeing excellently with those obtained in the sodium hydroxide electrolyte.

(c) SODIUM FORMATE ELECTROLYTE.

Twenty-five cc. of the zinc sulphate solution were pipetted into the silvered platinum dish and 0.5 gram of sodium carbonate, dissolved in a little water, was added. Formic acid was run in until all the carbonate was dissolved and a few drops of acid remained in excess. This solution was then diluted to 125 cc., as

usual, warmed and electrolyzed. The first experiments showed that this electrolyte possessed a resistance so high that about 25 volts were required to produce a current of 3.5 amperes, and the heat evolved was excessive. The addition of increased amounts of sodium formate obviated this trouble. The preferable conditions are those of Experiments 5 to 8.

Zinc taken. Gram.	Na_2CO_3. Grams.	H.COOH (sp. gr. 1.22). cc.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.	No.
0.2490	0.4	3.0	3½	23	10	0.2447	1
0.2490	0.6	3.5	4	20	10	0.2460	2
0.2490	2.5	3.5	5	10	20	0.2478	3
0.2490	2.5	3.5	5	10	20	0.2482	4
0.2490	5.0	4.6	5	8	20	0.2489	5
0.2490	5.0	4.6	5	8	20	0.2486	6
0.2490	5.0	4.6	5	8	20	0.2490	7
0.2490	5.0	4.6	5	8	20	0.2490	8

The zinc deposits were bluish gray in color and resembled those from the sodium hydroxide electrolyte, being fine-grained and very adherent.

(D) POTASSIUM CYANIDE ELECTROLYTE.

The results obtained with this electrolyte were so unsatisfactory that it was abandoned.

THE RATE OF PRECIPITATION OF ZINC FROM THE VARIOUS ELECTROLYTES.

These experiments were conducted precisely as those already described, save that at the end of the allotted time the liquid in the dish was very hastily siphoned off and the circuit interrupted as promptly as possible. Since the metal contained in the solution was not all deposited, it was impossible to allow much time for washing while the current was passing, nor, on the other hand, was it proper to interrupt the circuit at the instant of expiration of the desired time, thus leaving the acid liquor in contact with the deposits. A compromise was effected by the use of a large siphon which emptied the dish in a few seconds, the current being reduced to 1 ampere, and the liquid rapidly replaced by distilled water, after which the circuit was opened. The dish was then washed, dried and weighed as usual. The results for the first few minutes can be only approximate at best, as the metal was then being deposited very rapidly and the few seconds occupied in siphoning affected them considerably.

SODIUM FORMATE ELECTROLYTE.

Zinc taken. Gram.	Na_2CO_3. Grams.	$H.CO_2H$ (sp. gr. 1.22). cc.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.	No.	Speed.
0.2490	5	4.6	5	10	1	0.0839	1	I
0.2490	5	4.6	5	10	2	0.1418	2	I
0.2490	5	4.6	5	10	3	0.1723	3	I
0.2490	5	4.6	5	10	5	0.2095	4	I
0.2490	5	4.6	5	10	7	0.2244	5	I
0.2490	5	4.6	5	10	10	0.2464	6	I
0.2490	5	4.6	5	10	12	0.2483	7	I
0.2490	5	4.6	5	10	15	0.2490	8	I
0.2490	5	4.6	5	10	20	0.2490	9	I
0.4780	5	4.6	5	17	1	0.0990	10	II
0.4780	5	4.6	5	17	2	0.1721	11	II
0.4780	5	4.6	5	17	3	0.2738	12	II
0.4780	5	4.6	5	17	4	0.3398	13	II
0.4780	5	4.6	5	17	5	0.3916	14	II
0.4780	5	4.6	5	17	7	0.4430	15	II
0.4780	5	4.6	5	17	10	0.4595	16	II
0.4780	5	4.6	5	17	12	0.4638	17	II
0.4780	5	4.6	5	17	15	0.4603	18	II
0.4780	5	4.6	5	7	20	0.4522	19	II
0.4780	5	4.6	5	17-5	10 + 5	0.4688	20	II-o
0.4780	5	4.6	5	17-5	10 + 20	0.4753	21	II-o

With the intermediate speed, II, the pressure needed to produce 5 amperes was about 17 volts; this caused considerable heating and should be avoided if 0.25 gram of zinc or less be present, but when depositing larger quantities of metal the higher speed was preferable, as better deposits resulted. After about twelve minutes at this voltage the solution boiled freely from the heat evolved by the current and a visible re-solution of the metal sometimes took place. It was thought unnecessary to agitate the electrolyte during the entire time of deposition, as the greater part of the metal came down in the course of the first ten or twelve minutes, and the small amount of zinc remaining in solution would not be apt to come down in a spongy condition if the agitation were omitted; moreover, the lessening of the voltage required diminished the heat produced. Accordingly, in the above series of experiments in 20 and 21 the motor was stopped after ten minutes and the voltage lowered to such a value as would maintain the current at 5 amperes, that being the current employed during agitation. It was found that from 17 to 20 volts were needed while the anode was rotated, while 5 volts sufficed after

the anode became stationary. The last four observations, noted above, indicate that this suggestion is useful. With a lower speed of rotation the precaution is probably superfluous.

In the last twelve experiments there was used a zinc solution of which 25 cc. contained 0.2390 gram of metal. It was employed also in the two series next following.

SODIUM HYDROXIDE ELECTROLYTE.

Experiments upon the rate of deposition from this electrolyte yielded the following figures:

Zinc taken. Gram.	NaOH. Grams.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.	No.	Speed.
0.2490	6	5	8	1	0.0827	1	I
0.2490	6	5	8	2	0.1378	2	I
0.2490	6	5	8	3	0.1991	3	I
0.2490	6	5	8	4	0.2129	4	I
0.2490	6	5	8	5	0.2254	5	I
0.2490	6	5	8	7	0.2466	6	I
0.2490	6	5	8	10	0.2480	7	I
0.2490	6	5	8	15	0.2488	8	I
0.2490	6	5	8	20	0.2490	9	I
0.4780	6	5	6	1	0.1028	10	I
0.4780	6	5	6	2	0.1847	11	I
0.4780	6	5	6	3	0.2921	12	I
0.4780	6	5	6	4	0.3498	13	I
0.4780	6	5	6	5	0.4217	14	I
0.4780	6	5	6	7	0.4691	15	I
0.4780	6	5	6	10	0.4740	16	I
0.4780	6	5	6	12	0.4780	17	I
0.4780	6	5	6	15	0.4774	18	I
0.4780	6	5	6	10 + 20	0.4777	19	I
0.4780	6	5	6	20 + 10	0.4780	20	I

SODIUM ACETATE ELECTROLYTE.

Experiments upon the rate of deposition of zinc from this electrolyte gave the following figures:

Zinc taken. Gram.	$NaC_2H_3O_2$. Grams.	$HC_2H_3O_2$ (30 pct.) Drops.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.	No.	Speed.
0.4780	3	6	4	12½	1	0.0933	1	I
0.4780	3	6	4	12½	2	0.1500	2	I
0.4780	3	6	4	12½	3	0.2326	3	I
0.4780	3	6	4	12½	4	0.2957	4	I
0.4780	3	6	4	12½	5	0.3773	5	I
0.4780	3	6	4	12½	7	0.4645	6	I
0.4780	3	6	4	12½	10	0.4736	7	I
0.4780	3	6	4	12½	12	0.4725	8	I
0.4780	3	6	4	12½	15	0.4766	9	I
0.4780	3	6	4	12½	20 + 40	0.4779	10	I

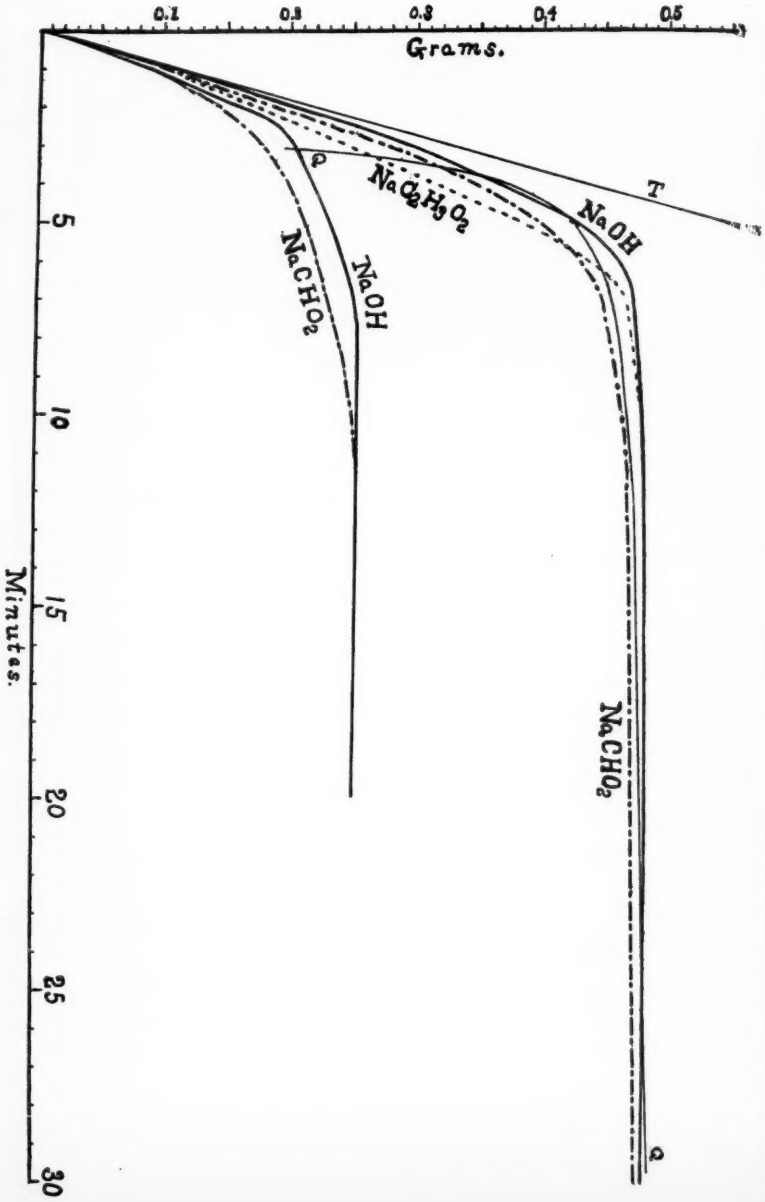
The above series of results may be expressed graphically, the number of minutes being used as the abscissa and the amount of metal deposited as the corresponding ordinate.

It will be noted that the graphs approximate the locus of the curve marked Q...Q, which is of the general form $[x\,y = c]$, an equilateral hyperbola, showing that after the first three minutes the amount of zinc deposited per minute decreases as the time increases. The straight line marked T represents the rate of deposition of zinc from a solution containing an unlimited amount of metal and is calculated from the electrochemical equivalent of zinc, in accordance with Faraday's law. This indicates that in the experiments in which nearly 0.5 gram of zinc was present at the outset, the current was depositing very nearly its maximum amount of metal during the first two minutes. The deposition curves thus appear to approach T at first, and later to approximate Q.

THE ELECTROLYTIC DETERMINATION OF THE ZINC CONTENT OF ZINC BLENDE.

The following experiments were conducted with a sample of very pure blende from Joplin, Missouri.

The mean of concordant gravimetric and volumetric determinations of its zinc content showed the presence of 65.70 per cent. of metal. For the determinations in the electrolytic way exactly 0.5000 gram of the powdered blende was weighed off, brushed into a No. 5 porcelain dish, moistened with water and covered with nitric acid (sp. gr. 1.41) and warmed gently on a stove plate. After about twenty minutes no further action appeared to take place and the glass cover was raised sufficiently to permit the escape of fumes and the liquid rapidly evaporated to dryness. The contents of the dish were then covered with pure hydrochloric acid (sp. gr. 1.21) and carried to dryness, and this treatment with hydrochloric acid repeated, care being taken to avoid overheating and consequent volatilization of zinc chloride. The dry salts were then moistened with strong hydrochloric acid and taken up in hot water. This operation occupied in all about one hour and ten minutes. Every sample of blende was treated in precisely the same manner.


0.1
0.2
0.3
0.4
0.5
Grams.
T
NaOH
$NaC_2H_3O_2$
Q
$NaCHO_2$
NaOH
$NaCHO_2$
Q
5
10
15
20
25
30
Minutes.

(A) SODIUM HYDROXIDE ELECTROLYTE.

The filtrate from the gangue was received in a small beaker and a solution of 6 grams of sodium hydroxide added, thereby precipitating the iron and redissolving the zinc as sodium zincate. This solution was filtered and the filtrate received in the silver-plated weighed platinum dish. The contents of the filter-paper were repeatedly washed with boiling water and the solution finally diluted to 125 cc. and electrolyzed, employing the conditions recommended in the earlier part of this paper, *viz.*, 5 amperes, 5 volts and speed I. The results were:

Blende taken. Gram.	Zinc found. Gram.	Zinc found. Per cent.
0.5000	0.3119	62.38
0.5000	0.3178	63.56
0.5000	0.3049	60.98
0.5000	0.3091	61.82
0.4000	0.2461	61.53
0.4000	0.2450	61.25

Suspecting the lack of concordance to be due to the presence of chlorides, the filtrate from the gangue was evaporated with sulphuric acid till fumes appeared, then taken up in water and treated as above. The results indicate that the chlorides present were not the disturbing factor.

Blende taken. Gram.	Zinc found. Gram.	Zinc found. Per cent.
0.5000	0.3131	62.62
0.5000	0.3088	61.76

An examination of the iron precipitates from the above samples of blende showed that they contained zinc in every case. It was found impossible to precipitate the ferric hydroxide free from zinc hydroxide by the use of sodium hydroxide as precipitant, and further study of this method of obtaining the zinc in a form suitable for electrolysis was abandoned.

An effort was made to omit the filtration of the iron precipitate and to electrolyze the solution of the sodium zincate in the presence of the suspended ferric hydroxide. An anode in the form of a platinum cylinder, suspended by a stout wire through its major axis and capable of rotation, was employed together with a semi-cylindrical cathode of platinum foil. The preliminary experiments showed the method to possess little of promise, and further study of it was postponed.

(B) AMMONIUM CHLORIDE ELECTROLYTE.

The thought arose that the solution of the blende containing the iron and zinc as chlorides might be treated with a solution of ammonium chloride and ammonium hydroxide, the ferric hydroxide being filtered off and the ammoniacal filtrate electrolyzed after the addition of an excess of sodium hydroxide, employing the conditions previously described under "sodium hydroxide electrolyte." Preliminary experiments with a solution of zinc sulphate of known strength gave excellent results, showing that ammonium chloride is not a disturbing factor.

Zinc taken. Gram.	HCl (sp. gr. 1.21). cc.	NH_4OH (sp. gr. 0.95). cc.	NaOH. Grams.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.
0.2390	5	Sufficient	6	5	6	20	0.2396
0.2390	5	to make	6	5	6	20	0.2393
0.2390	5	ammoniacal	6	5	6	20	0.2388

Further study demonstrated that the addition of the sodium hydroxide was unnecessary, the filtrate from the iron precipitate being a good conductor, if plenty of ammonium chloride was present, and it yielded up its zinc readily and completely on electrolysis. Wrightson noted the separation of zinc in an ammoniacal solution long ago; the failure of Reinhardt and Ihle to obtain satisfactory deposits from a solution containing free ammonia was probably due to the absence of agitation.

Zinc taken. Gram.	HCl (sp. gr. 1.21). cc.	NH_4OH (sp. gr. 0.95). cc.	NH_4Cl. Gram.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.
0.2387	5	25	1	5	5	20	0.2382
0.2387	5	25	1	5	5	20	0.2383
0.2387	5	25	1	5	5	20	0.2388
0.2387	5	25	1	5	5	20	0.2394

Fearing that the anode might be attacked by the chlorine liberated in contact with it, the platinum spiral was weighed before and after each of the above experiments, but it was found to have experienced no sensible change in weight.

Having thus found a new and most satisfactory elctrolyte, 0.5000 gram samples of the powdered blende were accordingly decomposed, as already described, and having removed the gangue and ferric hydroxide, the filtrate from the latter was received in the usual silvered and weighed platinum dish, the precipitate

not being washed with water. The dish was now set aside and the porcelain dish in which the iron had been precipitated was placed under the funnel and the iron precipitate washed into it with dilute hydrochloric acid and the acid washed out of the paper with hot water. The iron was then reprecipitated in the same manner as at first and filtered on the same paper, the filtrate being received in the platinum dish. This precipitate was now thoroughly washed with boiling water and then the latter added to the filtrate to make it up to the usual 125 cc., if any further dilution were needed.

Careful study showed that more than two precipitations of the iron were not required in the case of a blende similar to that used in this investigation. The iron precipitate was invariably free from zinc and the solution free from iron. It was found convenient to use in the above operations a total of 10 cc. of hydrochloric acid (sp. gr. 1.21), and enough ammonium hydroxide (sp. gr. 0.95) to neutralize this and yield about 2 cc. in excess. To the platinum dish containing the zinc solution was now added 0.5 gram of ammonium chloride, preferably in the dry form, since the solution by this time nearly equaled the 125 cc. The hot water used in washing rendered further heating unnecessary and the liquid was immediately electrolyzed. The deposits were crystalline, slightly coarse, but not spongy. They were light gray in color and sufficiently adherent to present no difficulty in washing, although less adherent than those obtained earlier in this study. These deposits will not bear rubbing with the finger.

Blende taken. Gram.	HCl (sp. gr. 1.21). cc.	NH_4OH (sp. gr. 0.95). cc.	NH_4Cl. Gram.	Amperes.	Volts.	Time. Minutes.	Speed.	Zinc found. Per ct.
0.5000	10	Sufficient	0.5	5	6	20	I	65.63
0.5000	10	to make	0.5	5	6	20	I	65.75
0.5000	10	strongly	0.5	5	6	20	I	65.73
0.5000	10	alkaline	0.5	5	6	20	I	65.65
0.5000	10		0.5	5	6	20	I	65.69
0.5000	10		0.5	5	6	20	I	65.68
0.5000	10		0.5	5	6	20	I	65.70
0.5000	10		0.5	5	6	20	I	65.69
0.5000	10		0.5	5	6	20	I	65.64

The time required to complete a determination of the zinc in blende by this method is about two hours and ten minutes from the time of weighing off the powdered ore to weighing its zinc content.

(C) SODIUM ACETATE ELECTROLYTE.

Attention was given to the precipitation of iron from blende as basic acetate and the electrolytic determination of the zinc in the filtrate, making use of the conditions given earlier for the use of an acetate electrolyte.

The blende having been decomposed, as described above, the solution containing the zinc and iron as chlorides was filtered off from the gangue and received in a No. 5 porcelain dish, nearly neutralized by sodium carbonate, 2.5 grams of sodium acetate added and the solution boiled for a few moments until the ferric basic acetate separated well. It was then filtered and the filtrate received in the usual silvered and weighed platinum dish. The precipitate was not washed, but was dissolved in dilute acetic acid and this solution allowed to run into the porcelain dish in which precipitation had been conducted before. The paper having been washed with hot water, this solution was nearly neutralized with sodium carbonate, 1 gram of sodium acetate added, and the precipitation made by boiling as before. This filtrate was received in the platinum dish and the iron redissolved and reprecipitated a third time. The combined filtrates were then made up to 125 cc. and electrolyzed.

Blende taken. Gram.	$NaC_2H_3O_2$. Grams.	$HC_2H_3O_2$ (30 pct). cc.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.	Zinc found. Per cent.
0.5000	3.5	1	5	13	25	0.3250	64.94
0.5000	3.5	2	5	13	25	0.3247	60.94
0.5000	4.5	0	5	13	25	0.3285	65.70
0.5000	4.5	0	5	13	30	0.3286	65.72
0.5000	4.5	0	5	13	30	0.3281	65.62
0.5000	4.5	0	5	13	30	0.3283	65.66
0.5000	4.5	0	5	13	30	0.3285	65.70

In the first two experiments free acetic acid was added before electrolyzing. The results show that this was not desirable, as the filtrate is sufficiently acid after the basic acetate separation of the iron.

The total time of an analysis of blende by this procedure is about two hours and thirty minutes.

(D) SODIUM FORMATE ELECTROLYTE.

The manipulation in this case was similar to that in the case of (C). The blende having been decomposed as usual and the

gangue filtered off, the filtrate was received in a No. 5 porcelain dish and exactly 5 grams of dry sodium carbonate added. The dish was then covered to prevent loss by spattering, and 4 cc. of formic acid (sp. gr. 1.22) were run in. The solution was boiled and filtered hot into the weighed and silvered platinum dish. The unwashed precipitate was then rinsed back into the porcelain dish by 6 cc. of 1 : 10 formic acid and the paper washed; 5 grams of sodium carbonate were then added and the solution boiled, filtered into the platinum dish and the paper well washed. Two basic formate precipitations were found to be sufficient. To the contents of the dish were then added 2 cc. of the 1 : 10 formic acid and it was then heated nearly to boiling and electrolyzed. The deposits were excellent.

Blende taken. Gram.	Na_2CO_3. Gram.	HCOOH (sp. gr. 1.22). cc.	Amperes.	Volts.	Time. Minutes.	Zinc found. Gram.	Zinc found. Per cent.
0.5000	5.5	4.8	5	9	25	0.3284	65.68
0.5000	5.5	4.8	5	9	25	0.3281	65.62
0.5000	5.5	4.8	5	9	25	0.3298	65.96
0.5000	5.5	4.8	5	9	25	0.3289	65.78
0.5000	5.5	4.8	5	9	25	0.3295	65.90

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 87.]

ELECTROLYTIC SEPARATIONS POSSIBLE WITH A ROTATING ANODE.[1]

BY DONALD S. ASHBROOK.

Received July 11, 1904.

A YEAR ago, Exner,[2] working in this laboratory, demonstrated that by using a high current density and great pressure with a rotating anode it was possible to determine fourteen metals in the electrolytic manner much more rapidly than had ever been done previously. The deposits were, in all instances, most satisfactory. These results constituted an important advance in electrochemical analysis. The objection once put forward, that too much time was necessary in such work, was completely removed. Indeed, Exner's investigation has wholly revolutionized electro-analysis. However, there remained the question as to how far this procedure

[1] From the author's thesis for the Ph.D. degree.

[2] This Journal, **25**, 896.

would lend itself to the separations of the several metals. This point became the guiding thought in the investigation here presented.

The apparatus and method of procedure have been fully described and amply developed by Exner, so that they need not be again entered upon, but the separations which were successful and have value will now be described in such detail as to enable others to repeat them with certainty of success.

COPPER.

I. From Aluminum.

(*a*) *In Sulphuric Acid Solution.*—Dilution, 125 cc.; 0.1 cc. of sulphuric acid (sp. gr. 1.83); $N.D_{100} = 4$ to 5 amperes and 1 to 4.8 volts; time, ten minutes. Copper present, 0.2696 gram; aluminum, 0.2500 gram; copper found, 0.2696, 0.2696 and 0.2695 gram. On increasing the amount of sulphuric acid to 1 cc., the deposit was much smoother and more uniform.

(*b*) *In Nitric Acid Solution.*—Dilution, 125 cc.; 1 cc. of nitric acid (sp. gr. 1.43); $N.D_{100} = 3$ amperes and 4 to 5 volts; time, twenty minutes. Copper present, 0.2874 gram; aluminum, 0.2500 gram; copper found, 0.2873, 0.2874 and 0.2874 gram. The conditions given here were most satisfactory for copper in this electrolyte. The speed may range from 300 to 400 revolutions per minute.

(*c*) *In Phosphoric Acid Solution.*—Dilution, 125 cc.; 10 cc. of phosphoric acid (sp. gr. 1.085); 50 cc. of 10 per cent. solution of Na_2HPO_4; $N.D_{100} = 5$ amperes and 6 volts; time, ten minutes. Copper present, 0.2742 gram; aluminum, 0.2500 gram; copper found, 0.2741, 0.2742 and 0.2741 gram. These conditions gave the best deposits. They were spongy in appearance, but perfectly adherent and were washed with ease. On dissolving them in nitric acid and testing with an ammonium molybdate solution, a slight precipitate of ammonium phosphomolybdate was obtained in every case. The amount of phosphorus was so slight, however, that it would not affect the weight of the deposit materially.

II. From Antimony.

(*a*) *In Tartrate Solution.*—Dilution, 125 cc.; 8 grams of tartaric acid; 25 cc. of ammonia; $N.D_{100} = 5$ amperes and 5 volts;

time, ten minutes. Copper present, 0.2742 gram; antimony, 0.2500 gram. Nearly all of the antimony was precipitated with the copper.

III. From Arsenic.

(*a*) *In Ammoniacal Solution.*—Dilution, 125 cc.; 25 cc. of ammonia; 2.5 grams of ammonium nitrate; $N.D_{100} = 5$ amperes and 7 volts; time, fifteen minutes. Copper present, 0.2742 gram; arsenic, 0.2500 gram; copper found, 0.2740, 0.2741 and 0.2741 gram. The deposit was dark in color, smooth and adherent.

(*b*) *In Nitric Acid Solution.*—The conditions were the same as were used in the separation of copper from aluminum. Copper present, 0.2742 gram; arsenic, 0.2500 gram; copper found, 0.2741, 0.2742 and 0.2742 gram.

IV. From Cadmium.

(*a*) *In Nitric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2742 gram; cadmium, 0.2500 gram; copper found, 0.2742, 0.2742 and 0.2742 gram.

V. From Chromium.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2890 gram; chromium, 0.2500 gram; copper found, 0.2890, 0.2891 and 0.2890 gram. Better deposits were obtained by starting with a current of 3 amperes, increasing gradually to 5 amperes.

(*b*) *In Nitric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2874 gram; chromium, 0.2500 gram; copper found, 0.2874, 0.2875 and 0.2874 gram. If the current was allowed to run above 3 amperes, the deposit weighed too high. A blank was run with chromium alone under the same conditions. It gave 0.0022 gram of a metal showing all the tests for chromium.

(*c*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2742 gram; chromium, 0.2500 gram; copper found, 0.2742, 0.2740 and 0.2742 gram. Slight traces of phosphorus were detected in the deposits.

VI. From Cobalt.

(*a*) *In Nitric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2874 gram; cobalt, 0.2500 gram; copper found, 0.2875, 0.2874 and 0.2874 gram. Cobalt was partially precipitated in the sulphuric acid and phosphoric acid electrolytes.

VII. From Iron.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2696 gram; iron, 0.2500 gram; copper found, 0.2694, 0.2695, 0.2696, 0.2696 and 0.2695 gram.

(*b*) *In Nitric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2874 gram; iron, 0.2500 gram; copper found, 0.2873, 0.2875 and 0.2874 gram.

(*c*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2742 gram; iron, 0.2500 gram; copper found, 0.2743, 0.2741 and 0.2742 gram; with 8 amperes in five minutes, Cu = 0.2741 gram. Slight traces of phosphorus were found in the deposits of copper.

VIII. From Lead.

(*a*) *In Nitric Acid Solution.*—The results were low, as lead seems to hold back the last traces of copper.

IX. From Magnesium.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2696 gram; magnesium, 0.2500 gram; copper found, 0.2696, 0.2696 and 0.2695 gram.

(*b*) *In Nitric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2874 gram; magnesium, 0.2500 gram; copper found, 0.2874, 0.2874 and 0.2875 gram. If the current was too high, a white deposit was obtained which dissolved in sulphuric acid without effervescence. A neutral solution of magnesium nitrate, acidified with 1 drop of nitric acid and electrolyzed with a current of 2 to 3 amperes and 15 volts for twenty minutes, gave a white coating, weighing 0.0334 gram.

(*c*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2742 gram; magnesium, 0.2500 gram; copper found, 0.2742, 0.2740 and 0.2742 gram.

X. From Manganese.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2890 gram; manganese, 0.2500 gram; copper found, 0.2890, 0.2891 and 0.2890 gram.

(*b*) *In Nitric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2874 gram; manganese, 0.2500 gram. Copper found, 0.2872, 0.2874 and 0.2874 gram. Only a part of the manganese was deposited as peroxide on the anode, but floating particles were not observed in the liquid.

XI. From Nickel.

(*a*) *In Sulphuric Acid Solution.*—No satisfactory deposits were obtained. All conditions were tried. The nickel seemed to hold the copper back when they were present in equal amounts. When the copper was greatly in excess, it carried the nickel down with it.

(*b*) *In Nitric Acid Solution.*—See the thesis of Exner.

(*c*) *In Phosphoric Acid Solution.*—Nickel was partially deposited in this electrolyte.

XII. From Uranium.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2890 gram; uranium, 0.2500 gram; copper found, 0.2889, 0.2890 and 0.2890 gram.

(*b*) *In Nitric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2742 gram; uranium, 0.2500 gram; copper found, 0.2742, 0.2741 and 0.2742 gram.

XIII. From Zinc.

(*a*) *In Sulphuric Acid Solution.*—Dilution, 125 cc.; 1 cc. of sulphuric acid (sp. gr. 1.83); $N.D_{100} = 3$ to 5 amperes and 5 volts; time, ten minutes. Copper present, 0.2890 gram; zinc, 0.2500

gram; copper found, 0.2890 gram, 0.2889, 0.2889, 0.2890 and 0.2888 gram. The current was increased gradually. The deposits were excellent.

(*b*) *In Nitric Acid Solution.*—See the thesis of Exner.

(*c*) *In Phosphoric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2635 gram; zinc, 0.2500 gram; copper found, 0.2635, 0.2633 and 0.2634 gram. Slight traces of phosphorus were found in the deposits of copper.

CADMIUM.

I. From Aluminum.

(*a*) *In Sulphuric Acid Solution.*—Dilution, 125 cc.; 1 cc. of sulphuric acid (sp. gr. 1.83); $N.D_{100} = 5$ amperes and 5 volts; time, ten minutes. Cadmium present, 0.2727 gram; aluminum, 0.2500 gram; cadmium found, 0.2728, 0.2727 and 0.2727 gram. The deposits were excellent, although slightly spongy, but perfectly adherent.

(*b*) *In Phosphoric Acid Solution.*—Dilution, 125 cc.; 10 cc. of phosphoric acid (sp. gr. 1.083); 50 cc. of a 10 per cent. solution of disodium hydrogen phosphate; $N.D_{100} = 5$ amperes and 7 volts; time, ten minutes. Cadmium present, 0.3032 gram; aluminum, 0.2500 gram; cadmium found, 0.3031, 0.3032 and 0.3032 gram. These deposits all showed slight traces of phosphorus.

II. From Chromium.

(*a*) *In Sulphuric Acid Solution.*—A beautiful silver white crystalline deposit of cadmium was obtained, which always weighed low.

(*b*) *In Phosphoric Acid Solution.*—The same conditions were observed as in the separation of cadmium from aluminum. Cadmium present, 0.3600 gram; chromium, 0.2500 gram; cadmium found, 0.3603, 0.3600 and 0.3600 gram.

III. From Cobalt.

(*a*) *In Sulphuric Acid Solution.*—Cobalt was partially precipitated in this electrolyte, and also in a phosphoric acid solution.

IV. From Iron.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium

present, 0.3032 gram; iron, 0.2500 gram; cadmium found, 0.3031, 0.3032 and 0.3032 gram.

(*b*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.3032 gram; iron, 0.2500 gram; cadmium found, 0.3032, 0.3031 and 0.3032 gram.

V. From Magnesium.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were observed as in the separation of cadmium from aluminum. Cadmium present, 0.2727 gram; magnesium, 0.2500 gram; cadmium found, 0.2727, 0.2728 and 0.2727 gram.

(*b*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.2727 gram; magnesium, 0.2500 gram; cadmium found, 0.2725, 0.2727 and 0.2727 gram.

VI. From Manganese.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.3600 gram; manganese, 0.2500 gram; cadmium found, 0.3600, 0.3599 and 0.3600 gram.

(*b*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.3600 gram; manganese, 0.2500 gram; cadmium found, 0.3600, 0.3601 and 0.3600 gram.

VII. From Nickel.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.2727 gram; nickel, 0.2500 gram; cadmium found, 0.2727, 0.2727 and 0.2726 gram.

(*b*) *In Phosphoric Acid Solution.*—The nickel was partially precipitated in this electrolyte.

VIII. From Zinc.

(*a*) Zinc always came down with the cadmium in sulphuric acid solution and also in the phosphoric acid solution.

SILVER.

From Aluminum.

(*a*) *In Nitric Acid Solution.*—Dilution, 125 cc.; 1 cc. of nitric acid (sp. gr. 1.43); $N.D_{100} = 3$ amperes and 3.5 volts; time, fifteen

minutes. Silver present, 0.2600 gram; aluminum, 0.2500 gram; silver found, 0.2600, 0.2599 and 0.2600 gram. The deposits obtained in this electrolyte were very poor. The addition of ammonium nitrate helped matters but little. Great care was necessary in washing not to lose some of the deposit.

With the conditions given for the separation of silver from aluminum, the former was quantitatively separated from cadmium, chromium, cobalt, iron, lead, magnesium, manganese, nickel and zinc.

It was also tried to effect the separation of silver from a number of other metals in a potassium cyanide electrolyte. No success was attained. The successful separations with mercury were those with aluminum and magnesium. Failures resulted in the case of iron, nickel, cobalt, zinc, manganese and cadmium. The electrolytes tried were sulphuric acid and nitric acid. Other separations are in progress.

ON THE STRUCTURE OF ALLOYS. PART I. ALUMINIUM ALLOYS.[1]

BY WILLIAM CAMPBELL.

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THE ALLOYS OF COPPER AND ALUMINIUM.

Previous Investigations.—Richards[2] describes the color of these alloys and gives the melting-points as determined by Le Verrier. He states that the natural compounds of aluminium and copper are those with the formulas $AlCu_3$ and Al_2Cu_3, and goes on to describe them. He says that the sharp fall in the melting-point at 37.5 per cent. aluminium indicates the alloy Al_3Cu_2, and remarks that it is a singular fact that the addition of copper to aluminium, in amounts up to 10 per cent., *lowers* the melting-point of the latter about 4° for every per cent. of copper present.

If the figures given by Le Verrier be plotted, we have a curve showing a drop to a minimum from pure copper to the 7.5 per cent. aluminium alloy, followed by a rise to a summit at the 10 per cent. alloy, then a sudden drop (with two slight halts) from this point at

[1] Read before the New York Section of the American Chemical Society, January 8, 1904.

[2] "Aluminum," p. 535, et seq (1896 ed.).

1029° C. to the 62.5 per cent. copper alloy at 545° C. Then follows a slight rise to 553° C. at 50 per cent. copper followed by a regular fall to 527° C. at the 33 per cent. alloy. Now, if we omit the reading of 528° C. as that of the 20 per cent. alloy, for it is certainly incorrect, the rest of the curve consists of a rise to aluminium. In other words, the curve consists of two summits at 50 per cent. and 90 per cent. copper, and three minima at 33 per cent., 62.5 per cent., and 92.5 per cent. copper, and the natural explanation would be that the summits represent compounds, the minima eutectics. So, if the 50 per cent. alloy represents a compound and the 33 per cent. copper alloy were the eutectic of that compound and aluminium, we should naturally suppose that the curve from aluminium to the 33 per cent. copper alloy would show a fall for each addition of copper, just as the freezing-point of water is lowered progressively with each addition of salt, until at —22° C. we reach the eutectic point, with 23.5 per cent. of sodium chloride. There is apparently no conclusive reason why the two alloys corresponding to Al_3Cu_2 and Al_2Cu_3 should be taken as definite compounds.

Le Chatelier, in a paper on the "Fusibility of Metallic Alloys,"[1] gives the freezing-point curve of the series, which is very smooth and regular. It shows two maxima, the one at 50 per cent. copper (or about 30 per cent. in equivalents), the other at 88 per cent. copper (or 75 per cent. in equivalents), and three minima, at 33 per cent. copper (or about 18 per cent. equivalents), at 54.5 per cent. copper (or 34 per cent. equivalents) and at 90.5 per cent. copper (or 80 per cent. equivalents). He concludes that two definite compounds are indicated, *viz.*, Al_2Cu (54 per cent. copper) and $AlCu_3$ (87.6 per cent. copper), which places the first almost at the minimum point at 54.5 per cent. copper. He says that these results agree with the previous determinations of Le Verrier.[2] They contradict the conclusions at which he had arrived from a chemical study of the alloys,[3] when he had isolated something corresponding to AlCu by hydrochloric acid or potassium hydroxide from an alloy with an excess of aluminium. These crystals were certainly altered by the reagents used. The formation of two compounds gives rise to three eutectics.

[1] *Bull. de la Soc. d'Enc.*, 1895. p. 569.
[2] Lejeal : *l'Aluminium*, p. 168.
[3] "On Definite Compounds in Metallic Alloys," *Compt. Rend.*, **120**, p. 835.

In a paper on the "Dilatation of Metallic Alloys," Le Chatelier[1] explains why the maximum points of the curves of fusibility do not always correspond exactly to a composition of the melted portion identical to the composition of definite chemical compounds to which these maximum points are supposed to owe their existence. Van der Waals[2] verified Le Chatelier's results and based his reasoning on the chemical equilibriums of W. Gibbs, which show that, to each maximum point of a curve of fusibility, there must necessarily correspond a composition of the liquid portion identical to that of the solid portion falling out of solution. This contradiction between theory and experience disappears if, starting from the definite compound, we consider the solid portion to constitute a solid solution.

When an alloy is made up by the juxtaposition in variable proportion of two well-defined constituents, a metal and a combination for instance, the dilatation of the alloy will necessarily be intermediate between those of the two components; if, on the contrary, the dilatation of the alloy has a very different value, it may be inferred that the alloy is a solid solution.

In the case of the alloys of aluminium and copper the compound $AlCu_3$ is quite normal, both as regards fusibility and dilatation curves. The compound Al_2Cu exhibits a maximum melting-point corresponding to 30 per cent. copper in equivalents differing from that of the definite compound, 33 per cent. The dilatation curve exhibits between these two percentages a very steep fall, which seems to indicate the existence of a solid solution.

In a former paper on the "Alloys of Aluminium"[3] a freezing-point curve was given very similar to that of Le Chatelier, but containing many lower points in addition. The maximum in the neighborhood of 50 per cent. copper was thought to indicate the compound Al_5Cu_2, but the results of microscopic research seem to show that this is not the case. The microscope shows that the horizontal line denoting the eutectic should be continued on to about 2 per cent. copper.

The microstructure of the copper-aluminium alloys has been studied by Le Chatelier[4] by means of a diffusion alloy. Five

[1] *Compt. Rend.*, June, 1899; *Bull. de la Soc. d'Enc.*, 1899, p. 900; *Metallographist.* **2**, p. 334.

[2] *Archives des Sciences néerlandaises*, 1899.

[3] W. Campbell and J. A. Mathews: This Journal, **24**, 265.

[4] *Metallographist*, **4**, p. 18.

distinct zones were seen. At the top are found grains and dendrites of aluminium passing down into the eutectic. When they disappear, well-defined crystals of Al_2Cu appear and the eutectic gradually diminishes until the whole mass is homogeneous. Below this, crystals, probably of AlCu, come in and are surrounded by a ground-mass of Al_2Cu. Then follow similar crystals in a eutectic alloy of minute structure. When these disappear, crystals of $AlCu_3$ come in and are seen surrounded by the eutectic.

Léon Guillet[1] prepared a series of alloys by reducing pure copper oxide with metallic aluminium. By dissolving out the ground-mass with hydrochloric acid he obtained crystals of $AlCu_3$ (87.11 to 87.75 per cent. copper, and AlCu (69.3 to 69.8 per cent. copper). The compound Al_2Cu was isolated by nitric acid and analyzed, 53.85 and 53.7 per cent. copper. In theory these three compounds require 87.55, 70.13 and 54 per cent. copper. He found that the compound AlCu contained 2 to 3 per cent. of residue, insoluble in concentrated nitric acid. It proved to be a compound of silicon, copper and aluminium.

Microscopic Examination.—The series lying between 0 and 52 per cent. copper presents no great difficulty. The freezing-point curve is made up of two inclined branches: The one starts from pure aluminium, showing an average fall of 3.75° C. for every per cent. of copper added; the other starts from the maximum at about 50 per cent. copper at 580° C., showing an average fall of almost 2.5° C. for every per cent. of copper decreased. These two branches meet at 535° C. at about 32 per cent. copper, and through this point the horizontal line, denoting the solidification of the eutectic, runs from about 2 to about 50 per cent. copper. Thus, between 0 and 32 per cent. copper the alloys consist of two constituents: The one is aluminium, which freezes out when the temperature of the alloy reaches that of the inclined branch, or "liquidus" curve, and continues to separate out, thus enriching the mother-liquor in copper until at 535° C. the latter contains 32 per cent. copper, when it freezes as the eutectic, the second constituent, whose solidification produces the evolution of heat marked by the horizontal line through 535° C., or the "solidus" curve.

Between 52 per cent. and 32 per cent. copper the alloys consist of two constituents; the compound Al_2Cu which freezes out when

[1] *Bull. de la Soc. d'Enc.*, **2**, 236 (1902).

the temperature reaches the "liquidus" and enriches the mother-liquor in aluminum until it has the composition of the eutectic, namely, about 32 per cent. copper. This occurs at 535° C. as before, when the whole mass becomes solid, the solidification of this eutectic or ground-mass (the second constituent) being denoted by the horizontal line through 535° C., or the "solidus." Hence, from aluminium to the eutectic point we find the alloys consist of grains and dendrites of aluminium in an increasing eutectic. At 32 per cent. copper the alloy consists of the eutectic alone, and we have neither free aluminium nor the free compound, simply a fine mixture of flakes of aluminium and flakes of the compound. From the eutectic point to 52 per cent. copper we find crystals of the compound in a decreasing ground-mass of the eutectic. So we find in this region of the series only two phases—aluminium and the compound Al_2Cu.

DESCRIPTION OF SPECIFIC ALLOYS.

2.28 per cent. Cu, 97.72 per cent. Al. Hard and strong. Cuts well with sharp tool, but not with saw. Composed of well-packed grains of aluminium with discontinuous ground-mass. The latter is composite in only a few places; generally consists of $CuAl_2$ alone. A similar case is found in annealed low-carbon steel where the pearlite has become patches of cementite, due to the absorption of its ferrite by the neighboring ferrite grains. Best etching with potassium hydroxide or hydrochloric acid. Deep etching shows up boundaries of aluminium grains, also attacks their centers. Aluminium grains apparently contain some $CuAl_2$ in solid solution. Fig. 13 shows the slowly cooled alloy × 33 diam. etched with potassium hydroxide.

4.45 per cent. Cu, 95.55 per cent. Al. Hard and strong. Cuts better with the saw, but begins to cut with a gritty feel. Shows the same structure as the above, but the aluminium grains are more inclined to form dendrites; are larger, ground-mass continuous for the most part and resembles a coarse eutectic, but is not typical. Etching attacks aluminium of the eutectic most deeply, due probably to couple action.

Alloys containing 6.5 per cent. and 8.2 per cent. copper are similar to the above. The dendritic character of the aluminium and the amount of ground-mass, or eutectic, increase with the copper present. In the 8.2 per cent. copper alloy the eutectic approaches more nearly normal, though much free Al_2Cu is still seen; the alloy inclines to brittleness, cuts with a gritty feel, yet saws fairly well. The difference between the alloys up to say 9 per cent. copper is not marked, and lies in the structure and amount of the ground-mass, and in the etching of the grains and dendrites of aluminium.

12.5 per cent. Cu, 87.5 per cent. Al. Hard and tough. Cuts very gritty. Very easily cut with saw. Fracture of ingot is finely granular, inclined to be fibrous. Slowly cooled it is more coarsely granular, resembling the structure of impure aluminium. On etching with dilute nitric acid, irregular grains and dendrites are seen in a continuous matrix. Ground-mass contains more of the compound than the typical 32 per cent. alloy, due to absorption of some aluminium by the dendrites. The slowly cooled alloy is seen in Fig. 1, magnified 35 diameters vertical illumination ($\times$ 35 v.). With increase in copper the alloys become harder, more gritty to cut and the fracture of the ingot becomes finer. With about 19 per cent. copper the ingot is strong, rings well, fracture is fine, dull and granular inclined to be fibrous, while the surface is covered with beautiful dendrites of aluminium, which are only about $^1/_{10}$ the size of those ordinarily found on the surface of an ingot of the pure metal.

23.8 per cent. Cu, 76.2 per cent. Al. Much weaker than the above; fracture is finer. A section shows well marked dendrites, some very large, set in the typical eutectic. In the cast alloy the fracture appears to have become coarser, because the dendrites of aluminium are now producing the regular ingot structure, due to growth perpendicular to the cooling surfaces (*cf.* fracture of cast zinc, antimony, etc.). Relative amount of eutectic seems less than in the slowly cooled alloy. Fig. 2, $\times$ 33 v., shows the slowly cooled alloy, etched with dilute nitric acid.

32 per cent. Cu, 68 per cent. Al. Fracture shows very large plate-like surfaces, while cavities show very good prisms with parallel growth, and faces covered with very small rounded knobs. Fracture fine, showing ingot structure very well, while on the surface is a well-marked hexagonal network of dendrites, especially along medial lines. The slowly cooled alloy shows the typical eutectic structure, together with fine black lines, along which fracture occurs, producing plate-like surfaces. A vertical section of the cast alloy shows a very curious dendritic growth of the compound more or less perpendicular to the cooling faces of the mold. This only extends for a short distance into the alloy and is apparently part of the eutectic, for under a high power it is seen that the structure is in places composed of parallel prisms, but each prism is composite (*i. e.*, is composed of Al and Al_2Cu) These will be mentioned again later. Fig. 3, $\times$ 35, obliquely illuminated ($\times$ 35 o.) shows the slowly cooled alloy; has a granular appearance, due to variation from fine to coarse, but where the aluminium is coarse the compound is coarse, for when a coarse granule of aluminium solidified a similar flake or granule of the compound solidified simultaneously alongside, that the composition of both the liquid and the solid might remain constant and equilibrium might be maintained.

A further increase in copper brings in the compound Al_2Cu, which has been isolated by Le Chatelier. The compound increases with the copper present, forming first isolated rods and prisms, then well-defined prisms, showing marked parallel growth until at 52 per cent. copper the whole mass becomes homogeneous. As the compound in theory requires 54 per cent. copper, the difference must be due to aluminium in solid solution. Le Chatelier's explanation of the 54 per cent. alloy melting at a lower temperature than that with, say, 4 per cent. less copper (in other words, the freezing of Al_2Cu at a point near a minimum of a curve) being due to the formation of solid solutions may be correct, but some recent experiments seem to indicate that the depression at 54 per cent. copper was due to surfusion, for all our readings were taken without stirring. If that be so, then the curve would rise uniformly from 32 per cent. to 54 per cent., then would take a sharp rise to 90 per cent. copper and there would be no depression at 54 per cent. This would give a curve much more easily explained. It is proposed to take a new series of pyrometric readings in this series.

37 per cent. Cu, 63 per cent. Al. Hard and brittle. Cuts well with a saw. The fracture shows a fine bright crystalline structure quite different from those alloys between 0 and 32 per cent. copper. Cavities are lined with beautiful prismatic and needle-like crystals, with marked parallel growth. A section etched with dilute nitric acid shows crystals of the compound, black to purple, with distinct orientation, or larger, more isolated prisms, set in the eutectic. The latter varies from fine to coarse, and in places is seen in the form of distinct prisms, usually round a cavity. The compound is often surrounded by an envelope of aluminium (*cf.*, slowly cooled CuAg alloys). When cast, the fracture shows good ingot structure, built up of similarly orientated dendrites of the compound, while the surface is covered with a network of dendrites similar to those met with in alloys of tin and antimony, containing about 10 per cent. tin. In section the ingot shows very beautiful designs, due to the marked geometrical orientation of the dendrites of the compound. Fig. 14, $\times$ 33 v., shows this alloy. The compound is seen as sections of crystals, which etch black and which occur in long trains with definite orientation. In Fig. 15 are seen several isolated prisms. The eutectic in places shows a distinctly dendritic structure. Fig. 19 shows a vertical section of the cast alloy, in which can be seen the dendrites of the compound in long, parallel trains. In each case etching was with dilute nitric acid.

44 per cent. Cu, 56 per cent. Al. Brittle, coarsely crystalline with cavities lined with prismatic needles in parallel growth. Are larger than in the last alloy. In sections very perfect crystals of the compound are seen; grow in groups of similarly orientated prisms. Are best seen under oblique illumination. The

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

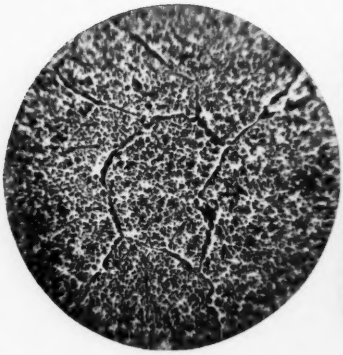

Fig. 7.

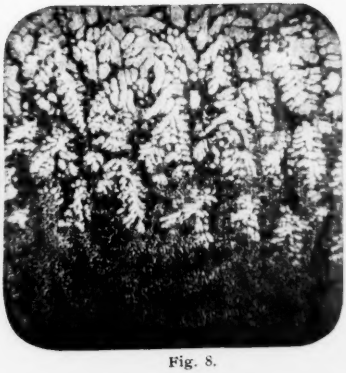

Fig. 8.

Fig. 9.

Fig. 10.

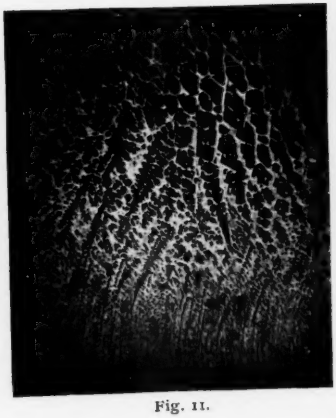

Fig. 11.

Fig. 12.

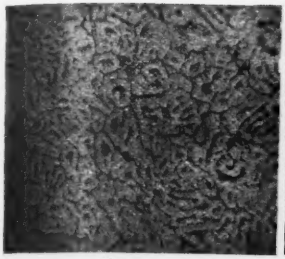

Fig. 13.

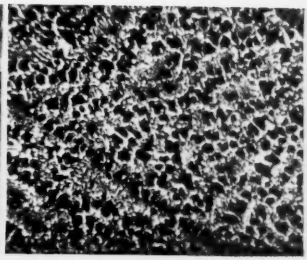

Fig. 14.

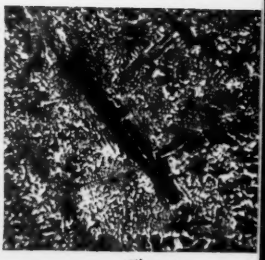

Fig. 15.

Fig. 16.

Fig. 17.

Fig. 18.

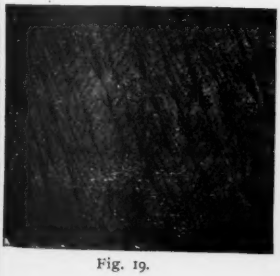

Fig. 19.

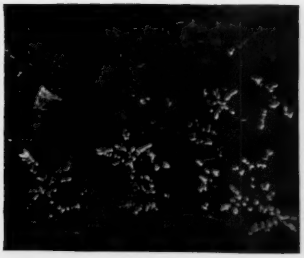

Fig. 20.

Fig. 21.

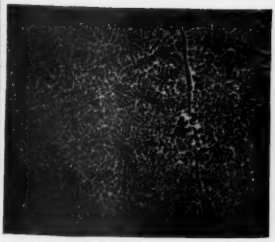

Fig. 22.

Fig. 23.

Fig. 24.

Fig. 25.

Fig. 26.

Fig. 27.

Fig. 28.

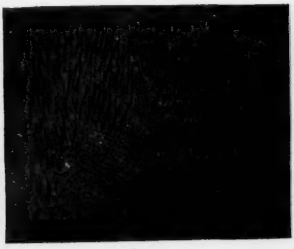

Fig. 29.

Fig. 30.

Fig. 31.

Fig. 32.

Fig. 33.

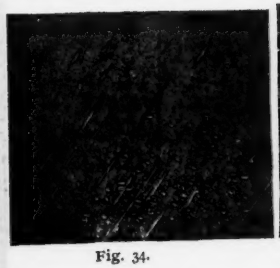

Fig. 34.

Fig. 35.

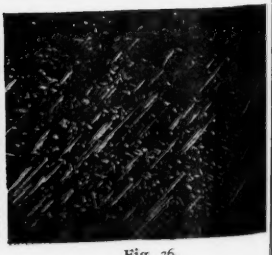

Fig. 36.

eutectic shows almost dendritic aluminium in places, also black lines, but these are smaller than in the 32 per cent. alloy. When cast, is hard and brittle, with a coarsely crystalline bright fracture, which shows prisms under the microscope. A section shows the compound in parallel groups of short prisms, similarly orientated in each group, giving a very decided ingot structure. Ground-mass in places, composed of aluminium alone where the crystals of the compound are closely packed. Fig. 4 shows the alloy slowly cooled, × 30 o., while Fig. 16 shows the same when cast, × 33 o. Three separate groups of the black prisms are seen surrounded by a ground-mass of the eutectic.

47 per cent. Cu, 53 per cent. Al. A very coarse, whitish fracture, with large shining faces. In sections the compound is seen in prisms, which now interfere and are surrounded by the eutectic, as before. The cast alloy shows a bright crystalline fracture with well-marked ingot structure, due to the prisms. Fig. 17, × 30 v., shows the slowly cooled alloy, lightly etched. In addition to the compound and the eutectic, long needles are seen. These are not attacked after long etching and are probably the silicide of copper and aluminium found by Guillet They were noticed in small quantity in many of the alloys containing Al_2Cu.

51 per cent. Cu, 49 per cent. Al. Has a beautiful shining fracture, showing, in places, very large and long prisms in parallel groups. A longitudinal section of one of these shows very little eutectic, which lies as a cement between the massed prisms. When cast, the alloy forms a bright ingot with a glistening whitish fracture, which is coarse and shows prisms. The surface structure of the ingot is composed of the basal planes of these prisms, which stand in relief owing to the shrinkage of the liquid portion on cooling. The structure resembles that of bismuth. In sections the massed prisms of the compound are found to be similarly orientated and there is very little ground-mass between them, showing that we have almost reached a homogeneous alloy. The prisms etch much deeper in the center than at the outside, which seems to point to their containing some aluminium in solid solution. Fig. 18, × 16 v., shows the surface structure of an ingot, with the prisms standing out in relief.

54 per cent. Cu, 46 per cent. Al. Hard brittle alloy with a fracture similar to the last, but more hackly; shows some prisms in cavities. In sections we find the massive compound, which is evidently built up of massed prisms, whose boundaries show out as lines. At the base of the alloy a section showed a few bright white grains and dendrites, evidently the first appearance of a new constituent. The ingot is brittle with a hackly fracture. Fig. 20, × 35 v., shows the slowly cooled alloy deeply etched with dilute nitric acid, which has blackened the compound $CuAl_2$, but left the bright white dendrites unattacked. Under a higher power numerous fine white dots can also be seen, similar to the dendrites.

From 54 per cent. copper onwards, the freezing-point curve consists of a very steep rise to a summit at about 90 per cent. copper at 1055°. There are several marked subsidiary points, but these were so slight that no definite conclusions could be drawn from them. The compound $AlCu_3$ is indicated by the summit (87.6 per cent. copper) and has been isolated by Le Chatelier. It remained for the microscope to determine the constitution of the intermediate alloys, and by its means the following results were obtained:

As the copper is increased above 54 per cent. the fine white dendrites grow larger and become more numerous. They swell out and become large, extended grains, while the ground-mass of Al_2Cu decreases. At 70 per cent. copper there is still a comparatively large amount of ground-mass, but AlCu, isolated by Guillet, contains 70 per cent. copper, which seems to point to the fact that we are dealing with a series similar to the SbSn series, in which Stead[1] found that between 7.5 and 40 per cent. antimony, cubes of SbSn crystallize out in a ground-mass of tin containing antimony in solid solution. Above 40 per cent. antimony the cubes no longer are pure SbSn, but are richer in antimony, and the alloy corresponding to SbSn (*i. e.*, 50.21 per cent. antimony) consists of crystals + ground-mass.

At 75 per cent. copper and 25 per cent. aluminium there is still a trace of the matrix, the color of the series having changed from white to a steely blue. From 78 to 83 per cent. copper, or from Al_2Cu_3 to $AlCu_2$, the alloys are homogeneous, become more reddish in tinge and tend towards a glassy conchoidal fracture. Hence we might say that between these limits we have solid solutions of either of these compounds and that below, say 70 per cent. copper, the compound isolated, corresponding to AlCu, was really Al_2Cu_3 or $AlCu_2$, containing a fixed amount of Al_2Cu in solid solution. The fact remains that the alloy corresponding to AlCu is not homogeneous.

57 per cent. Cu, 43 per cent. Al. Still shows a whitish hackly fracture. A section shows narrow white bands and dendrites in a dark structureless ground-mass when etched with nitric acid. Without etching, the ground-mass has a slightly lighter color than the dendrites which are inclosed in it. Fig. 5, × 33 v., shows the slowly cooled alloy etched with nitric acid.

65 per cent. Cu, 35 per cent. Al. Has a hackly fracture of a darker shade than the above. Under the microscope a mass of irregular cloud-like rosettes and a few stray dendrites are seen in the darker etching ground-mass. The cast alloy is brittle, with a bluish gray color and is composed of closely packed rough dendrites in parallel groups set in the darker etching ground-mass.

67 per cent. Cu, 33 per cent. Al. Similar alloy of bluish gray color. Is hard and brittle, with a tendency to sub-conchoidal fracture. By polishing alone the alloy is seen to be composed of

[1] *J. Soc. Chem. Ind.*, 1897, pp. 200 and 506.

bluish tinged cloud-like grains, surrounded by a yellowish white ground-mass (Al_2Cu). The ground-mass is much softer than the grains, which polish in relief. On etching with nitric acid the ground-mass turns brown to black, while the grains are attacked, but not evenly. The cast alloy is hard, with a sub-conchoidal fracture. The surface shows very small feathery dendrites of hexagonal type in relief. In sections we have a similar structure to the slowly cooled, but, of course, much finer. The grains oxidize in the atmosphere much more than the ground-mass. Fig. 6, × 33 v., shows the slowly cooled alloy, etched with nitric acid and gives the characteristic structure of the cloud-like grains.

70 per cent. Cu, 30 per cent. Al. Bluish gray, with a fracture similar to the last. On polishing, the alloy shows the same bluish grains surrounded by the lighter matrix. On etching, the ground-mass turns brown to black, as before. Under oblique light the dendrites appear white, for they have been attacked, while the ground-mass is a dead-black. The only difference between the two alloys is that here we have less of the ground-mass (Al_2Cu), as we should expect. The cast alloy is also similar and shows irregular grains surrounded by an envelope of the lower compound. The grains etch before the ground-mass, which blackens only. Hence we see that the alloy corresponding to the formula CuAl is composed of two constituents.

75 per cent. Cu, 25 per cent. Al. Very brittle, of a bluish tinge. When etched with nitric acid and examined under a low power it is seen to be coarsely crystalline, like a compound or a pure metal. Under a high power the last traces of the white constituent, or ground-mass, are seen filling a few isolated interspaces between the grains. Many of the grains have a banded structure, like twinning or that due to strain in some metals. The surface, when deeply attacked, shows innumerable small negative crystallites, more or less lath-shaped.

80 per cent. Cu, 20 per cent. Al. Very hard, brittle, of a reddish tinge. Only one constituent can be seen; even when deeply etched the alloy appears homogeneous. When cast the alloy shows a very coarse ingot structure, but there is no second constituent. The alloy resembles $SnCu_3$.

83.26 per cent. Cu, 16.74 per cent. Al. Very hard, of a distinctly reddish tinge, coarsely crystalline, each grain etching out with dotted lines as boundaries and being built up of secondary grains. When cast, has a bright, glassy, almost conchoidal fracture, with reddish tinge. A section shows good ingot structure on etching, with dotted lines showing up the borders of the primary grains, which, under a high power, are built up of fine secondaries. No second constituent can be seen, though its beginning is indicated by the etching of the boundaries of the grains.

From this point, corresponding to $AlCu_2$ onwards, the alloys are very complicated. According to Le Chatelier the fusibility curve consists of a continued rise to a summit at $AlCu_3$, followed by a slight fall to a minimum at 90 per cent. copper and then a uniform rise to the melting-point of pure copper. Our own curve is similar in shape. The meaning of the fall is uncertain and when the evidence of the microscope is considered it seems probable that we ought to have a smooth curve from 83 per cent. copper to pure copper, or at all events two curves which make an obtuse angle and show no fall. As in our curve, this fall is only from 15° to 20° C., it may have been caused by surfusion. The microscope and heat treatment show that between 83 per cent. and about 90 per cent. copper the alloys solidify as homogeneous solid solutions, which, at a lower temperature, rearrange themselves in a manner directly comparable to steel or the copper-tin alloys from Cu_4Sn onwards. The eutectoid point is about 87 per cent. copper, as compared with pearlite with 0.8 per cent. carbon, or the copper-tin eutectoid at 75 per cent. copper. The slowly cooled alloys between 84 per cent. copper and 87 per cent. copper consists of decreasing amounts of a compound poorer in copper (probably $AlCu_2$); those between 87 per cent. and about 90 per cent. copper consist of increasing amounts of a compound richer in copper (which Le Chatelier found to be $AlCu_3$), set in the eutectoid. On reheating any of these alloys to a bright red and quenching, a structure is produced similar to martensite of quenched steel, while by annealing the quenched alloy for a short time the original structure is restored. The complete cooling curve for the series must, therefore, show a V-shaped curve between 83 and 90 per cent. copper at some distance below the "solidus," and similar to that denoting the separation of ferrite and cementite in steel, or of $SnCu_4$ in the copper-tin alloys. On account of its steepness it is probable that it will only be determined by differential cooling curves.

From 90 per cent. copper onwards the color of the alloys changes from yellow to red with a corresponding change in structure as the dendrites of copper come in, the alloys being solid solutions.

85 per cent. Cu, 15 per cent. Al. Shows a marked change in color to a reddish straw. Fracture sub-columnar. A section shows two constituents; large granular structure (Fig. 7, × 16 v., etched by nitric acid), each grain being bounded by black veins and filled with black irregular rosettes and dendrites, surrounded by a white ground-mass. The structure is very similar to that of a 70 per cent. copper and 30 per cent. tin alloy. The cast alloy is brittle, with a glassy fracture. Shows an ingot structure and on etching is seen to be composed of the black compound and light ground-mass, like the slowly cooled alloy. Fig. 21, × 33 v., shows the structure of the cast alloy. Under a high power in each case the ground-mass has a eutectoid structure, with a marked segre-

gation of the light constituent on the borders. On reheating to a bright red and quenching, the original structure is destroyed, and under low powers the alloy appears homogeneous, while by reheating again and slowly cooling, a structure similar to the original is reproduced. Fig. 22, × 35 v., shows the alloy after quenching, reheating and slowly cooling in the air. The structure is now even clearer than the original. Now, seeing that these changes took place far below the melting-point of the alloy, they must be changes in the solid, and the ground-mass is, therefore, not a eutectic, but a eutectoid like pearlite.

87 per cent. Cu, 13 per cent. Al. Eutectoid, and therefore consists entirely of the ground-mass, whose composite structure can only be seen under high powers. On reheating and quenching it assumes a structure resembling martensite, while annealing restores the original.

88.5 per cent. Cu, 11.5 per cent. Al. Decidedly yellow color. A crack showed dendritic structure, due to the original cooling of the solid solution. On etching a section, the ground-mass or eutectoid is attacked, leaving light yellow needles and fine grains in relief. The ground-mass has a comparatively coarse granular structure, whose boundaries are shown by the marked orientation of the yellow needles. Fig. 24, × 33 v., shows this alloy. Le Chatelier found the yellow needles to be $AlCu_3$ (87.6 per cent. copper), but they evidently contain more copper than this, for they must contain more copper than the whole alloy. The cast alloy shows a splendid columnar structure when broken. It is very tough and cuts well. In section the columnar structure is explained, for the alloy is built up of long grains or columns perpendicular to the cooling faces. Each grain has a lighter border, due to the segregation of needles of the compound from the solid solution. Fig. 23, × 33 v., shows the cast alloy, in which cooling was too rapid to allow the solid solution to completely rearrange itself into the yellow constituent and the eutectoid. If the alloy be reheated to a bright red and quenched, a structure like martensite is produced as before, while annealing restores the original, showing the original was due to change in the solid.

89.5 per cent. Cu. 10.5 per cent. Al. A similar alloy in appearance, fracture, etc. A section shows the effect of the slight increase in copper by the increase in size and quantity of the yellow constituent. Fig. 25, × 35 v., shows the slowly cooled alloy. It is composed of lighter grains in a darker ground-mass, which is the eutectoid. There is a marked contrast when compared with the last alloy. When cast, the structure of the alloy depends entirely on the thickness of the ingot, or rather on the rate of cooling. In no case was a structure like Fig. 23 found. Where the ingot was thin, its structure × 100 is represented by Fig. 24, while a thicker ingot would show a structure similar to this, but much coarser. Again, when quench-

ing the alloy to produce the martensitic structure, it is necessary to heat this alloy to a higher temperature than that required by the last (just as the refining temperature of a 0.35 per cent. carbon steel is much higher than that of steel with 0.75 per cent. carbon), because the yellow granular constituents begin to separate out at a much higher temperature.

91 per cent. Cu, 9 per cent. Al. Hard, tough, light yellow, very strong. When a section is etched, it is seen without using a lens to be built up of grains or crystals, each of which in turn is built up of dendrites whose orientation varies from grain to grain. Under the microscope a discontinuous ground-mass is seen, but is in very small amount, and even under high powers has no distinct structure. The dendrites, on the other hand, are not uniform in composition, for they etch at the center, or core, to a darker color than at the outside. In other words, they are richer in copper at the center, due to diffusion not being sufficient to produce a state of equilibrium. In all cases so far the copper-rich cores have made their appearance before the ground-mass has disappeared, which shows that we are dealing with solid solutions and not a pure compound, $AlCu_3$. When cast, the alloy is hard and yellow, with a fine columnar fracture. A section shows that this is due to casting, for each elongated grain or crystal is built up of dendrites like those of the slowly cooled alloy, but very much finer; the ground-mass is discontinuous as before.

94 per cent. Cu, 6 per cent. Al. Very tough, golden yellow, of a very coarse structure, which can be seen by the eye on etching. It is built up of huge dendrites like copper, etching differentially (*i. e.*, deeper in the centers, or cores, and progressively less to the outside), which shows we are dealing with solid solutions whose compositions vary uniformly from edge to center of the dendrites, becoming richer in copper. The ground-mass seen in the 91 per cent. copper alloy has gone, the whole mass being built up of dendrites isomorphous with copper. Fig. 26, $\times$ 15 o., shows the alloy, etched with hydrochloric acid. If ammonium hydroxide be used, the structure is shown up by a beautiful series of colors, similar to those produced by heat-tinting. The cores are most deeply colored: brown, red and violet; the edges are green, straw and white.

96.3 per cent. Cu, 3.7 per cent. Al. Hard, tough, darker yellow, shows a splendid dendritic structure to the eye when etched, like the 94 per cent. alloy. The whole structure is very coarse. There is no second constituent, but differential etching shows that we have a solid solution which is not in equilibrium. When cast the structure is similar, but smaller, and is built up of dendrites definitely arranged. Fig 27, $\times$ 16 v., shows a vertical section through a small ingot. The difference in shade between the centers and boundaries of the dendrites is marked. Their cubic character resembles that of copper.

97.1 per cent. Cu, 2.9 per cent. Al. Tough, reddish yellow, huge grains and dendrites, which etch very differentially. Fig. 28, × 33 o., shows the typical structure on etching with hydrochloric acid. Cast alloy is strong and tough, with a reddish columnar fracture. A section shows a structure similar to the last alloy, but with the dendrites less pronounced and the granular structure more marked, owing to the better orientation, as is shown in Fig. 29, × 16 v.

A further increase in copper gives similar alloys until at 100 per cent. we have the structure of pure copper. In dealing with the series from about 92 per cent. copper onwards acid of a considerable strength is necessary to bring out the structure of these solid solutions. Hydrochloric acid blackens the cores and leaves the edges of the dendrites bright. Nitric acid attacks the edges most, the cores next and the intermediate zone least of all. Ammonium hydroxide produces beautiful oxidation tints, which show the cores dark and the edges light.

DIFFUSION ALLOYS.

In order to make sure that no important change had been overlooked and to confirm previous results, ten or more diffusion alloys were made by pouring molten aluminium on to molten copper or a molten aluminium-rich alloy on to one containing more copper and allowing the whole to slowly solidify, thus obtaining by diffusion an alloy which varied uniformly in composition from top to bottom.

0 to 52 per cent. Cu. At the top the alloy shows massed grains of aluminium. On passing downwards the eutectic appears and increases; the aluminium grains become smaller, change to dendrites and finally disappear at the eutectic ratio, 32 per cent. Cu, 68 per cent. Al. Fig. 8, × 35 v., etched with dilute nitric acid shows this section. Below this point crystals of the compound (Al_2Cu) come in and increase as the eutectic decreases, until at about 52 per cent. copper, the whole mass is composed of the compound. Fig. 9, × 35 v., etched with dilute nitric acid, shows this change in structure. Two points were noticed: The eutectic area forms a broad band across the alloy and *if* the alloy varies uniformly in composition it would seem to show that the eutectic could vary in composition within certain small limits. Again, at the aluminium end, the eutectic shows a relatively large amount of the compound, while at the lower (copper aluminium) end it shows a relatively greater amount of aluminium. This is due to absorption of aluminium by aluminium dendrites and of Al_2Cu by the crystals of the compound. A similar thing happens in the AgCu series and other alloys.

54 to 80 per cent. Cu. At the top of this range the alloy is homogeneous and very brittle, being composed of Al_2Cu. As

we pass down, grains and rods of the new constituent come in and increase with the copper content. The ground-mass of Al_2Cu decreases, the grains, etc., become dendrites, which change to cloud-like masses, while finally at the base of the series the whole mass is homogeneous once more.

80 to 100 per cent. Cu. Starting at the top of this range we have a homogeneous mass as at the base of the last. Etching with nitric acid as before, or with hydrochloric acid, shows this black. Passing down, a whitish ground-mass soon appears and surrounds the black crystals, which have definite boundaries. The ground-mass under high powers shows the composite structure of a eutectoid. The eutectoid increases, the black crystals decrease and become very fine dendrites and finally disappear when the whole mass is composed of the eutectoid at about 87 per cent. copper. Fig. 11, × 35, etched with dilute hydrochloric acid, shows this range, while the top of Fig. 10, × 33 v., shows the disappearance of the black dendrites. The eutectoid occupies a distinct band across the alloy and has a more or less linear structure in its central portion. Below this, bright yellowish needles of the higher compound come in. These increase in size and quantity, and the eutectoid diminishes, as is shown in the lower part of Fig. 10, × 33 v., etched with hydrochloric acid. Before the ground-mass entirely disappears it loses its eutectoid structure and in the center of the yellow grains dark etching cores appear. These increase and the ground-mass finally disappears. The change is shown in Fig. 12, × 33 v., etched with hydrochloric acid. This brings us to about 92 per cent. copper and from this point onwards the cores, rich in copper, increase in size and quantity till the mass becomes pure grains and dendrites of copper at 100 per cent. The change undoubtedly represents a series of solid solutions.

HEAT TREATMENT AND CHANGE OF STRUCTURE IN THE SOLID.

To show the changes round the eutectoid point a diffusion alloy ranging from 85 to 89 per cent. copper was made and very slowly cooled. At the top, dark etching crystals and dendrites were seen, surrounded by the eutectoid with a fine structure. These diminish and disappear near the center of the section, while the eutectoid assumes a very coarse structure (comparatively). Below this point needles and grains of the yellow constituent appear and increase, while the ground-mass assumes a finer, mottled structure. Fig. 30 shows the section near the top, with the dark dendrites set in the eutectoid. Fig. 31 is between the top and center, showing the disappearance of the black dendrites and the coarsening of the ground-mass, while Fig. 34 shows the section near the base, with the bright yellow needles and grains. In each case the magnification is 35 v., etched with ammonium hydroxide. The alloy was heated to a bright red and quenched. The original

structure was destroyed and a new one, resembling that of martensite of quenched steel, produced. Fig. 32, × 35 o., shows the structure of the quenched specimen from the top to the center, while Fig. 35, × 35 o., shows that near the base where very coarse polygons have developed, similar to those of martensite in much overheated and quenched steel. This shows that at the high temperature the whole series exists as a uniform solid solution, like martensite or the copper-tin alloys,[1] which have been so well worked out by Heycock and Neville. On reheating the quenched alloy to a bright red and cooling in the air the martensitic structure was, for the most part, destroyed and the original almost completely restored. At the top of the section black dendrites make their appearance and the appearance is similar to Fig. 31, but the whole structure is coarser. The center of the alloy shows a beautiful martensitic structure still, but it is much finer than that of the quenched specimen. Fig. 33, × 35 v., shows this new structure. At the base the original structure has been completely restored, as seen in Fig. 36, × 35 v. The reason why the central band of the eutectoid retained the martensitic structure on reheating was due to the fact that the cooling in air was too rapid to allow of complete change. A second reheating, followed by slow cooling in the furnace, removed all trace of it. A similar alloy was made, but was reheated to the melting-point and allowed to cool slowly in the furnace. In this way the range of composition varied from top to bottom from 86+ per cent. to 88.5 per cent. copper, or a little over 2 per cent. A section showed a coarse granular structure (polygonal grains) to the eye. At the top of the alloy a few black dendrites (like Fig. 31) were seen, but soon disappeared. The eutectoid occupied a comparatively broad band just above the center of the alloy, below which bright, thin needles, then grains of the yellow compound came in. At the base the structure was like Fig. 34. On reheating and quenching at a bright red, the whole mass became martensitic, exactly like the last alloy, while the base of the alloy showed a coarse granular structure, as before. On reheating and slowly cooling in the furnace the original structure was restored, the coarse grains due to the original cooling being even more marked, due to segregation around their boundaries. No sharp change in the eutectoid structure was met with, but, as before, it was noticed that, where neither of the constituents were present in the free state, the structure was most coarse. Both of these experiments show that between about 83 and 90 per cent. copper there are profound changes in structure, which take place in cooling, far below the "solidus."

The above work points to the following conclusions:

(1) The series between 0 and 54 per cent. copper forms a simple set of alloys with a eutectic point at about 32 per cent. copper.

[1] *Phil. Trans. Roy. Soc.* (London), A. **202**, 1-69.

Between 0 and 32 per cent. copper, grains and dendrites of aluminium occur in an increasing ground-mass; between 32 and 54 per cent. copper, crystals of the compound Al_2Cu occur in a decreasing ground-mass of the eutectic. In neither case are the dendrites or crystals pure but contain about 2 per cent. of copper,[1] or of aluminium, as the case may be, in solid solution.

(2) From 54 per cent. copper onwards we find a decreasing ground-mass of Al_2Cu, while a new constituent, in the form of dendrites and then irregular masses, increases until at about 78 per cent. copper the alloys are homogeneous.

(3) The alloys remain homogeneous from 78 per cent. to about 83 per cent. copper (from Al_2Cu_3 to $AlCu_2$).

(4) It is open to question whether this new constituent is AlCu, Al_2Cu_3 or $AlCu_2$, for in any case it forms solid solutions. There may even be two isomorphous compounds present.

(5) Above 83 per cent. to about 90 per cent. copper the alloys solidify as solid solutions, which, at a lower temperature, rearrange themselves, according as the alloy contains more or less than 87 per cent. copper—the eutectoid point. This change is similar to that which takes place in steel or in the bronzes.

(6) From 92 per cent. to 100 per cent. copper, the alloys form a series of solid solutions isomorphous with copper and show no rearrangement in the solid state.

In conclusion, my thanks are due to M. N. Bolles, Ph.D., who made several electrolytic copper determinations; to Professor Howe, in whose laboratory the work was carried out; and to Professor E. H. Miller, for his interest in the work.

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ON THE STRUCTURE OF ALLOYS. PART II. SOME TERNARY ALLOYS OF TIN AND ANTIMONY.[2]

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THE alloys of tin and antimony have been studied by Stead,[3] Behrens,[4] Reinders,[5] and others. Between 0 and 7.5 per cent. of

[1] This would probably be in solution as Al_2Cu.
[2] Read before the New York Section of the American Chemical Society, June 10, 1904.
[3] *J. Soc. Chem. Ind.*, March-June, 1897; December, 1898.
[4] *Verslagen d. Kon. Acad. v. Wetensch. te Amst.*, June 25, 1898, 58; and *Baumaterialkunde*, Vol. IV, Part 6 and 7 (*Metallographist*, Vol. III, p. 4).
[5] *Zischr. anorg. Chem.*, **25**, 113 (1900).

antimony we have a series of solid solutions of antimonide of tin in tin, whose structure is isomorphous with tin. Fig. 1, × 35 v., shows the alloy containing 5 per cent. antimony and 95 per cent. tin, and this is characteristic of this part of the series. The freezing-point curve shows a rise from pure tin at 232° C. to the 7.5 per cent. alloy at 256° C. (Stead), or to the 8 (molecular) per cent. alloy at 243° C. (Reinders).

Above 7.5 per cent. antimony hard, bright white cubes make their appearance. They are lighter than the mother-liquor out of which they crystallize and so they float to the top and form a layer there. Each addition of antimony produces an increase in the number and size of the cubes until at about 25 per cent. antimony they are found to reach the bottom of the alloy. Their shape is shown in Fig. 2, × 33 v., which is a horizontal section through the 20 per cent. alloy, etched with dilute nitric acid. The ground-mass is the same as the 7.5 per cent. alloy. These cubes continue to increase with the antimony present up to 40 per cent. when their form changes, and as the antimony increases they become plate-like, as seen in Fig. 3, × 16 o., which shows the alloy containing 45 per cent. antimony and 55 per cent. tin deeply etched. The composition of these crystals is in dispute. Stead found them to correspond to SbSn up to the 40 per cent. antimony alloy, but beyond that point they contain more antimony. Behrens, on the other hand, isolated them by another method and found them to be $SbSn_2$.

At 55 per cent. antimony the ground-mass disappears. On polishing, the mass appears homogeneous, but by deep etching harder cores are found within the plates. These increase with the antimony present, develop into well-defined antimony dendrites and finally occupy the whole field. Fig. 4, × 16 o., shows the 60 per cent. antimony alloy etched with nitric acid.

The cooling- or freezing-point curve, as determined by Reinders, shows some interesting points, for when the alloys contain more than 20 (molecular) per cent. antimony the cooling curves show three retardations, the middle one being feeble at 310° C. and the lower at 243° C., corresponding to the solidification of the ground-mass. From 51 to 60 (molecular) per cent. antimony the cooling curves show four halts. The first and second (430° C.) are well marked, the third and fourth (310° and 243° C.) are feeble and die out above this percentage. This shows that above

25 per cent. antimony the alloys become complex and are not the simple series with the single compound SbSn, as previous authorities have stated. Reinders concludes from his researches that tin and antimony form two solid solutions, tin containing a maximum of 11 per cent. antimony, and antimony containing an unknown quantity of tin. They also form two compounds: The cubic form, SbSn or $SbSn_2$; the plate-like form, Sb_4Sn_3 or Sb_3Sn_4. Until these two compounds have been isolated and analyzed their formulae can only be guessed at.

The importance of the ternary alloys of tin and antimony in the arts made it seem desirable to examine their structure. As a basis of study, the 25 per cent. antimony and 75 per cent. tin alloy was taken, because, in it, the bright cubes of SbSn (following Stead for convenience) are distributed throughout the whole mass of the alloy. For industrial purposes, such as bearings, etc., the antimony would not exceed 12 per cent., but in this case we would be dealing with comparatively rapid cooling. A large amount of the alloy was carefully made and cast. Convenient weights were then alloyed with 10 per cent. of the following metals: Lead, cadmium, bismuth, copper, silver, zinc, arsenic and aluminium. The melts were made in a small Fletcher gas-furnace. Ninety parts of the 25 per cent. antimony and 75 per cent. tin alloy were melted under potassium cyanide and then 10 parts of the third metal added. The alloy was well shaken around to produce a uniform liquid, and, shortly afterwards, the gas and air were shut off and the crucible allowed to cool down slowly in the furnace. In the case of aluminium, potassium cyanide cannot be used and charcoal was substituted. The alloys can be divided into groups according to their resulting structure.

Group I. The third metal forms a simple alloy with tin, and the whole consists of bright cubes of SbSn set in a ground-mass, which is composed of grains and dendrites of tin, surrounded by the eutectic.

10 per cent. Pb, 22.5 per cent. Sb, 67.5 per cent. Sn. Lead and tin form a simple series of alloys with a eutectic point 68 per cent. tin, melting at 180° C., and intermediate alloys are composed of grains and dendrites of tin or lead set in the eutectic. If the whole of the antimony present combines with tin to form SbSn (and this is likely for lead and antimony also form simple alloys whose eutectic point is at 12.5 per cent. antimony and melts

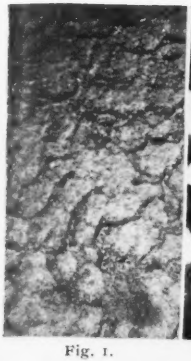


Fig. 1.

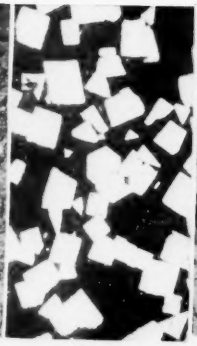
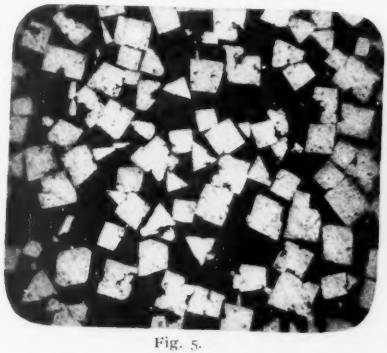


Fig. 2.

Fig. 3.

Fig. 4.



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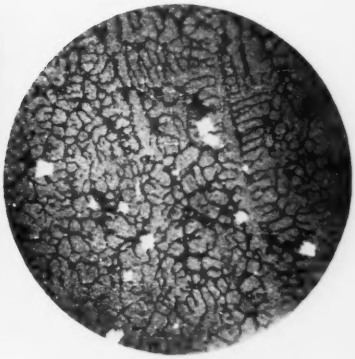

Fig. 6.

Fig. 7.

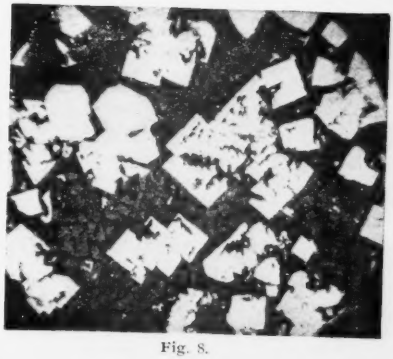

Fig. 8.

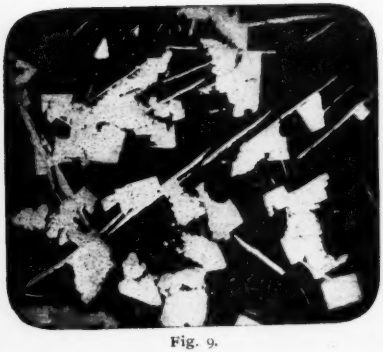

Fig. 9.

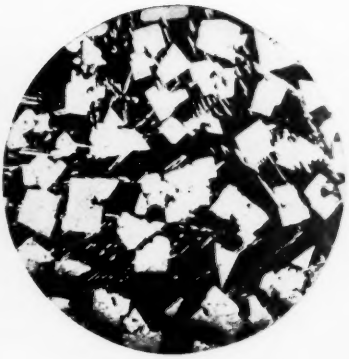

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.

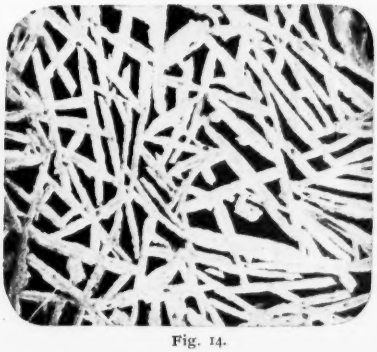

Fig. 14.

at 247° C.[1]) we should have a ground-mass consisting of 18 per cent. lead and 82 per cent. tin. This would give us an excess of tin which would crystallize out as large dendrites and be surrounded by a ground-mass of the eutectic. It is possible, however, that the ground-mass contains antimony and consists of dendrites of tin, surrounded by a lead-tin-antimony eutectic.

A section of the alloy was cut and polished. Etching with dilute nitric acid intensifies the contrast, but the structure can be seen after polishing alone. Bright white cubes, in all respects similar to SbSn, are seen, but they do not extend to the bottom of the alloy, having concentrated in the upper two-thirds by gravity where free. The attached ones remain in place round the base and sides of the alloy, of course. Fig. 5, × 38 v., etched with dilute nitric (5 per cent.) acid shows a section from near the top of the alloy. The cubes are seen set in a ground-mass, which is composed of two constituents. The structure of the ground-mass can best be seen at the base of the alloy from which the cubes have nearly all separated out and floated to the top. Fig. 6, × 38 v., shows this part of the section. A few stray cubes are still left, but the rest of the field is filled with comparatively large grains and dendrites of tin, surrounded by a dark ground-mass, which is apparently composed of alternate flakes of lead and tin and is the eutectic. From the manner of etching it would seem that the dendrites were not pure, but contained a certain small amount in solid solution.

10 per cent. Bi, 22.5 per cent. Sb, 67.5 per cent. Sn. Bismuth and antimony are said to form a series of isomorphous solid solutions like gold and silver. Bismuth and tin form a simple series of alloys with a eutectic at 58 per cent. bismuth, melting at 133° C. The dendrites of tin which separate out contain about 10 per cent. bismuth in solid solution, however. If, as before, the antimony combined with the tin to form SbSn, we should have a ground-mass of 18 per cent. bismuth and 82 per cent. tin, which would be formed of grains and dendrites of tin (10 per cent. bismuth in solid solution), surrounded by an envelope of the eutectic of Bi-Sn (58 per cent.). Fig. 7, × 38 v., shows a horizontal section of an alloy containing 10 per cent. bismuth, 28 per cent. antimony and 62 per cent. tin, etched with 5 per cent. nitric acid. It shows bright cubes whose parallel growth is very similar to

[1] Stead : *J. Soc. Chem. Ind.*, 1897, p. 203.

that found in a slowly-cooled 25 to 30 per cent. antimony, 75 to 70 per cent. tin alloy. Deep etching attacks these crystals much in the center and at a little distance from the edge, which seems to show that they contain either tin or bismuth in solid solution. The ground-mass is composed of black-etching grains of tin (10 per cent. bismuth in solution), surrounded by a brighter envelope. This has a pinkish tinge and is the BiSn eutectic, the tin of which has mostly migrated into the grains adjoining. Under a high power the black-etching grains of tin are seen to contain minute white dots of the color of SbSn, which seem to have been thrown out after solidification.

Group II. The third metal forms a compound with tin and the whole consists of cubes of SbSn and crystals of the new compound set in a matrix, which is the eutectic.

10 per cent. Ag, 22.5 per cent. Sb, 67.5 per cent. Sn. According to Charpy[1] silver and tin form a compound Ag_2Sn. Between 100 and 65 per cent. silver we have isomorphous mixtures of Ag and Ag_2Sn, while below this we have a simple series of alloys of Ag_2Sn and Sn with a eutectic at 3.5 per cent. silver, melting at 222° C.[2] Supposing the antimony all combines to form SbSn, the ground-mass would consist of 18 per cent. silver and 82 per cent. tin, and, therefore, would consist of crystals of Ag_2Sn set in the silver-tin eutectic. Fig. 9, × 38 v., shows the alloy. Bright cube-like forms of SbSn are seen, together with long needles and rods of the compound (characteristic of silver-tin alloys from 3.5 per cent. silver onwards) set in a ground-mass identical with the silver-tin eutectic. The freezing-point curve for silver and antimony is composed of two branches, the one from pure antimony to 55 per cent. silver, the eutectic point (485° C.) being quite normal, the other from pure silver having a decided angle at 72 per cent. silver, corresponding to the formula Ag_3Sb. Hence, by increasing the silver and decreasing the tin, points would be reached where either Ag_3Sb and SbSn or Ag_3Sb and Ag_2Sn would be found in the alloy.

5 per cent. Cu, 23.75 per cent. Sb, 71.25 per cent. Sn. Copper and tin form a eutectic at 1 per cent. copper, above which point to about 8 per cent. crystals of CuSn are found set in the eutectic. From 8 per cent. copper onwards the series is complicated by changes which take place after solidification has begun. The

[1] *Bull. de la Soc. d'Enc.*, March, 1897, p. 418.

[2] Heycock and Neville : *Phil. Trans. Roy. Soc.* (1897), 189 A.

series contains $SnCu_3$ and $SnCu_4$. If, as before, the antimony and tin combine, the rest of the alloy would be composed of about 9.5 per cent. copper and 90.5 per cent. tin, which would consist of needles and skeleton stars of CuSn in the copper-tin eutectic. Fig. 10, × 30 v., shows the alloy etched with 5 per cent. nitric acid. Bright white cubes are seen, together with needles giving a curious arrow-head shape in cross-section, surrounded by the dark ground-mass, which is apparently the copper-tin eutectic. It is noticed that some of the CuSn has solidified first of all and the SbSn has grown around it, resembling the ophitic structure of plagioclase and pyroxene in certain diabases.

The curve of fusibility of antimony and copper, as determined by Le Chatelier, consists of four branches, which cross at the two eutectic points at 25 and 71 per cent. copper. The summit occurs at 60 per cent. copper. Stansfield[1] has published a similar curve with a summit at 57 per cent. copper. According to Stead[2] there are two compounds in this region, $SbCu_2$, the purple compound, and $SbCu_3$, which is white. By varying the percentages of tin, copper and antimony we obtain alloys with the purple compound of copper and antimony. An alloy containing 16 per cent. tin, 56 per cent. copper and 48 per cent. antimony showed very coarse plates of the purple compound which had crystallized out first of all. Between these coarse plates the spaces were filled with white rods, or smaller plates of a white compound and a ground-mass, which is evidently a eutectic composed of needles of the purple and white compounds and white grains.

Group III. The third metal has a greater affinity for the antimony and forms a compound with it. If the whole of the antimony is combined, the ground-mass is an alloy of the third metal and tin; if some antimony remains over, the ground-mass is an antimony-tin alloy.

10 per cent. Al, 22.5 per cent. Sb, 67.5 per cent. Sn. Antimony and aluminium combine to form a compound SbAl (81.5 per cent. antimony), which solidifies at a slightly lower temperature than copper.[3] Tin and aluminium form a series of alloys in which aluminium crystallizes out in a ground-mass containing about 0.5 per cent. aluminium in solid solution. If the whole of the antimony combined with the aluminium to form SbAl, we should have left

[1] *Congrès Internationale de Physique*, Paris, 1900.
[2] *J. Soc. Chem. Ind.*, December, 1898, p. 1111.
[3] Gautier : *Bull. de la Soc. d'Enc.*, 1896 ; Campbell and Matthews ; This Journal, 1902

a ground-mass consisting of about 6 per cent. aluminium to 94 per cent. tin. This would be composed of dendrites of aluminium set in a tin-rich ground-mass isomorphous with tin. In making the alloy, great difficulty was met with. On adding the aluminium to the molten SbSn alloy combination immediately takes place and SbAl is formed which, on account of its high melting-point, makes the alloy very gritty. Potassium cyanide must not be used as a cover, for it attacks the alloy and makes an incoherent mass. By keeping the alloy melted for some time under a cover of charcoal, good results are obtained. Fig. 11, × 38 o., shows a section of the alloy lightly etched with nitric acid. Well-defined crystals of SbAl are seen set in the ground-mass composed of dendrites of aluminium in the matrix of tin (0.5 per cent. aluminium). Deep etching and slightly repolishing reveals the structure of the ground-mass. Fig. 12, × 38 v., etched with 2 per cent. nitric acid deeply and repolished to remove oxide, shows the crystals of SbAl in relief. The dendrites of aluminium are seen, set in the tin-rich ground-mass. On exposure to the atmosphere for a few weeks the alloy disintegrates to a black powder, due to oxidation.

10 per cent. Zn, 22.5 per cent. Sb, 67.5 per cent. Sn. The fusibility curve of zinc and antimony, as given by Gautier,[1] shows a summit near 64 per cent. antimony, with two eutectic points at about 4 per cent. and about 77 per cent. antimony. This would point to the formation of a compound, probably SbZn. Three alloys were made: 10, 50 and 95 per cent. antimony. The first showed needles, rods, and grains of a compound in a well-marked eutectic ground-mass. The second showed the massive crystals of the same compounds in the eutectic, while the last showed beautiful crystals of antimony in the second eutectic. A compound is certainly formed. Tin and zinc form a simple series, with the eutectic at 8 per cent. zinc, melting at a little above 200° C. If the zinc combined with the antimony to form the compound SbZn, a ground-mass would be left containing approximately 11 per cent. antimony and 89 per cent. tin, which would show cubes of SbSn in the tin-antimony solid solution. On examining the alloy three constituents can be seen. Hard cores or crystals which stand out in relief, surrounded by a softer white constituent, the whole being surrounded by a tin-rich ground-

[1] *Bull. de la Soc. d'Enc.*, 1896, p. 1293.

mass, isomorphous with tin. The harder constituent, apparently SbZn, often occurs free and the composite crystals are larger towards the top of the alloy. Fig. 13, × 30 v., shows a part of the alloy near the top. The fact that no cubes of SbSn are seen and that the second constituent always covers the zinc-antimony compound like an envelope and, as a rule, has the same form, would suggest that it was the result of a reaction between the liquid ground-mass and solid crystals of the SbZn compound. Further work is needed on this point.

10 per cent. Cd, 22.5 per cent. Sb, 67.5 per cent. Sn. According to Kapp[1] tin and cadmium form a eutectic at 70 per cent. tin to 30 per cent. cadmium. The alloys of antimony and cadmium do not appear to have been worked out. On alloying two parts of cadmium with one part of antimony, an alloy is produced consisting of massive crystals of a compound in a small amount of eutectic with a fairly coarse structure. The eutectic is apparently that of cadmium and the compound, and the compound probably contains more cadmium than CdSb. Fig. 8, × 30 v., shows the antimony-tin alloy with 10 per cent. cadmium. The view is from the upper part of the alloy and shows cube-like forms of SbSn, with which are mixed a few short prisms and irregular laths of a pinkish constituent set in a matrix which is isomorphous with tin. There is a slight layer at the base of the alloy in which no SbSn is seen, but where the other compound occurs in the tin-rich ground-mass. It seems probable that the cadmium and antimony have combined to form the pinkish compound, but unless this is rich in cadmium the amount formed would not account for all. On the other hand, the ground-mass under high powers is seen to differ from that of the typical SbSn alloys, for it contains light-colored dots and in places needles, and etches much more lightly; it may contain cadmium in solid solution. Lastly, an alloy containing arsenic was examined.

10 per cent. As, 22.5 per cent. Sb, 67.5 per cent. Sn. When arsenic is added to tin, thick rough plates are formed. These have been found by Stead to have a composition corresponding to Sn_3As_2, while the ground-mass solidifies at 235° C. and contains a trace of arsenic in solid solution. I have been able to find no reference to the alloys of arsenic and antimony. Fig. 14, × 38 v., etched with nitric acid, shows the 10 per cent. arsenic alloy. It

[1] *Ann. Phys. Chem.* [4], **6**, 754–773 (1901).

is of whitish color, very brittle, with a beautifully crystalline fracture. The section shows light-colored plates set in a matrix, which etches like the SbSn or SnAs solid solution. The plates form a regular network and are really composed of a harder, slightly colored core surrounded by a white envelope. There is a sharp line between the two. The outer portion is SbSn. This was proved by making a diffusion alloy. The 25 per cent. antimony and 75 per cent. tin alloy was melted and well covered with potassium cyanide. Massive arsenic was carefully dropped in and when melted the whole was allowed to slowly cool. The base of the alloy was the same as the typical 25 per cent. antimony and 75 per cent. tin, but the top was similar to Fig. 14, only coarser. On deeply etching, the cubes of SbSn were seen to pass up into and become part of the white outer constituent of the composite plates. The inner cores contain the arsenic, for they increase with the arsenic present. An alloy was made by adding arsenic to the SbSn alloy at a dull red heat until dense fumes came off. The alloy consisted of very coarse, thick plates, with very broad cores. The white envelopes were present in about the same amount as in the 10 per cent. alloy, but the ground-mass had greatly diminished, which would seem to show that the central cores were As_2Sn_3. The appearance of the envelopes of SbSn around the cores of the other constituent resembles that of the zinc alloy. They are both similar to composite crystals of Cu_3Sn and CuSn found in the copper-tin series,[1] which are caused by reaction of the mother-liquor on crystals of Cu_3Sn, which have formed at a higher temperature. In other words, they are due to imperfect equilibrium.[2] We may have such a case here, which will be ascertained when cooling curves have been obtained for these alloys.

The arsenic alloy was placed last because it is doubtful where it belongs.

The above examples show that by alloying the tin-antimony alloy with 10 per cent. of the third metal three types of structures may occur:

(1) Cubes of SbSn are found in a ground-mass of tin dendrites, surrounded by the eutectic of tin and the third metal: lead and bismuth.

[1] Campbell: *Proc. Inst. Mech. Eng.* (London), 1901. Appendix Alloys Research Committee Report.
[2] Heycock and Neville: *Phil. Trans. Roy. Soc.* (London), A **202**, 1-69.

(2) Cubes of SbSn and crystals of a compound of tin and the third metal are found set in the eutectic of tin and the second (new) compound: copper and silver.

(3) A compound of antimony and the third metal is formed; the ground-mass consists of (*a*) crystals of the third metal in its eutectic with tin: aluminum. (*b*) Crystals of SbSn and a tin-rich solid solution: zinc and perhaps cadmium.

Arsenic probably belongs to a sub-group of (2) where SbSn and crystals of a compound of tin and the third metal occur in a ground-mass, which is a solid solution of tin.

It may be that most of the eutectics are not binary, but contain the three metals; however, only two constituents apparently are revealed by the microscope.

It remains to run cooling curves on each of the alloys and as far as possible to isolate and analyze their harder crystalline constituents by which means more light would be thrown on their constitution. It is intended to expand the work by making similar series with different percentages of tin and antimony, and different amounts of the added metal, from which, it is hoped, much more may be learned of the constitution of these ternary alloys.

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THE VISCOSITY OF SOLUTIONS IN RELATION TO THE CONSTITUTION OF THE DISSOLVED SUBSTANCE.

BY ARTHUR A. BLANCHARD.

Received July 28, 1904.

WORK upon this theme was first undertaken by Mr. M. A. Stewart in the laboratories of the New Hampshire College. The method herewith described was worked out by him and was presented in June, 1903, together with a considerable amount of experimental data as a thesis for the Bachelor's degree at the above-named college. A brief account of his work was given by the author at the June, 1903, meeting of the American Chemical Society at Cleveland.[1] Since then the work has been further carried on, partly at that college and partly at the Massachusetts Institute of Technology. The author wishes to acknowledge his

[1] *Science*, **18**, 98 (July 24, 1903).

indebtedness to Prof. Charles L. Parsons, of the New Hampshire College, for many favors and for the interest shown by him in this work.

I. RELATION BETWEEN VISCOSITY AND MIGRATION VELOCITY IN SOLUTIONS OF ELECTROLYTES.

The theme of this article was first suggested by the striking relations between the migration velocities of various elementary ions and the viscosity of solutions of their salts. Wagner,[1] and notably Euler,[2] have shown that the viscosity effect of the individual ions increases regularly as the migration velocity decreases. Euler, indeed, has calculated so-called viscosity constants for a large number of ions and finds the relation between these and the migration velocities expressed by the following formula, to hold:

$$(A - 0.68) \cdot U = \text{konst},$$
$$\text{or } (K - 0.68) \cdot V = \text{konst},$$

where A and K are the viscosity constants and U and V are the rates of migration of the anion and cation respectively.

The value of *konst* for a series of fourteen different ions ranges between 18.7 and 22.4. The only ions studied which form exceptions to this rule are H- and OH-ions with values of *konst* 126.7 and 78.5 respectively.

The internal friction in a liquid undoubtedly depends, among other things, upon the mass of the rubbing particles. One would expect that the larger the mass of the ion the greater would be its friction to motion through a liquid, and hence, the smaller its rate of migration. Just the opposite, however, would appear to be actually the case if one compared the behavior of the ions in individual groups of the periodic system. Most markedly is this so in the group of the alkali metals, for which are copied the values from Euler's article.

Ion.	Migration velocity.	Viscosity constant.
Li	39.8	1.150
Na	49.2	1.091
K	70.6	0.962
Rb	73.5	0.958
Cs	73.6	0.949
NH_4	70.4	0.963

[1] *Ztschr. phys. Chem.*, **5**, 31 (1890).
[2] *Ibid.*, **25**, 539.

II. POSSIBLE EXPLANATION OF PECULIARITIES IN THESE PHENOMENA BY THE HYDRATE THEORY.

The possibility that *ions* may be not merely electrically charged atoms or atom groups, but rather these in combination with a greater or lesser number of solvent molcules, has often been suggested. Indeed, it is held by some, notably Werner, that electrolytic dissociation is to be accounted for largely upon this ground. If this then be true, it is not hard to suppose that the elementary atoms lowest in each group have the greatest power of holding solvent molecules in combination, so that, as a matter of fact, the hydrated *Li*-ion might have a greater mass than the other alkali metal ions.

III. NEGATIVE VISCOSITY AND THE HYDRATE THEORY.

It seems to us that this *Hydrate Theory* of the constitution of the ions offers an explanation of the remarkable phenomenon of *negative viscosity*, and that, by this phenomenon, the theory is, therefore, given more probability. The ions NH_4, *K*, *Rb*, *Cs*, *Tl*, and NO_3, when dissolved in water, tend to lessen the time of flow of a given volume of liquid under the same pressure through a capillary tube. Thus the solution of any salt of one of these ions will have a lesser viscosity than pure water, provided that the other ion of the salt have not a positive viscosity great enough to counterbalance the effect of the first ion.

Negative viscosity has been accounted for upon the ground of Electrostriction,[1] according to which a charged ion is surrounded by a strong electrical field which causes a compression of the liquid in this field. This accords well with the fact that a salt solution occupies a lesser volume than the dry salt plus pure water. According to Röntgen,[2] and Warburg and Sachs,[3] the viscosity of water is slightly decreased by pressures up to 150 atmospheres. Cohen[4] found that at 1° the viscosity is decreased to the extent of 6.28 per cent. by a pressure of 600 atmospheres. At 15° this decrease is but 2.33 per cent., while at 23° it is but 1.01 per cent. Hauser[5] found that at about 32° pressure ceases to affect the viscosity of water, while above 32° it causes an increase of vis-

[1] Drude and Nernst: *Ztschr. phys. Chem.*, **15**, 79 (1894).
[2] *Wied. Ann.*, **22**, 510 (1884).
[3] *Ibid.*, **22**, 514 (1884).
[4] *Ibid.*, **45**, 666 (1892).
[5] Drude's *Annalen*, **5**, 597 (1901).

cosity. Likewise the effect of salts with negative viscosity was found by Sprung[1] to become zero in the neighborhood of 32°, while above that temperature these salts caused an increase of viscosity. If there are not other objections to the Electrostriction hypothesis of negative viscosity, these facts afford it a strong confirmation.

If portions of solvent between charged ions are subjected to great pressure, due to the electric field, it seems quite as probable that the solvent so enmeshed between the ions would be mechanically dragged along with them, thus increasing the viscosity, as that the compression would decrease the viscosity.

From surface tension phenomena it seems probable that water consists of polymerized H_2O-molecules. If now ions exist as hydrates instead of simply as electrically charged atoms or radicals they must be built up at the expense of the polymerized water molecules. Now it would seem highly probable that some of the hydrated ions, $M.nH_2O$, might have a smaller mass, or, at least, a more symmetrical structure than the $(H_2O)_m$ molecules of pure water. In such a case there might well be less friction to their motion than to that of the molecules of pure water. It is important to note that complexes between undissociated molecules of solute and molecules of solvent may be formed, as well as the *solvates*[2] of ions.

With decreasing temperature the polymerization of water increases. The formation at least of some of the possible polymers is attended by an expansion (which between 4° and 0° C. exceeds the normal contraction). Pressure thus will lessen the amount of polymerization and also lessen the viscosity—since polymerization obviously causes increased viscosity. At 32° C. the critical point is reached, where the polymerization of water is so slight that it is not decreased by pressure. The formation of solvates takes place to a lesser extent the higher the temperature. At higher temperatures there are also fewer molecules of polymerized water whose concentration will be diminished by the formation of hydrates. At 32° the effect of certain salts in lessening the

[1] Pogg. *Ann.*, **159**, 1 (1876, Vol. 3).

[2] As complexes of solute with molecules of solvent are likely to occur with other solvents than water, and since the term hydrate could not, without confusion, be applied to these, it would seem desirable to have a special term by which they could be designated. The name solvate, suggested by Professor A. A. Noyes, seems to be very appropriate.

viscosity, as well as that of pressure, becomes zero. The facts then which seemed so strongly to support the explanation according to Electrostriction agree with equal closeness to the requirements of the Hydrate Theory.

IV. THE VARIATION OF VISCOSITY WITH CONCENTRATION.

The viscosity of liquids is customarily determined by flow through capillary tubes by the method of Poisseule and of Hagenbach. The absolute viscosity is given by Hagenbach's formula:[1]

$$\eta = \frac{\pi D r^4 t}{8 l V},$$

where η = the coefficient of viscosity, that is, the force in dynes necessary to maintain a liquid surface, of unit area, in motion, with unit velocity, past another equal and parallel surface at unit distance; D is the pressure necessary to overcome friction, that is, the actual pressure diminished by that pressure which would be necessary to give, to the liquid flowing through the tube, the kinetic energy which it possesses; r is the radius of the capillary; t is the time, and V the volume of liquid flowing in time t; l is the length of the capillary.

The viscosity of solutions is, however, commonly expressed in terms of the viscosity of pure water at zero, or at the same temperature, taken as unity. Of the several formulae proposed to express the viscosity of solutions in terms of the concentration, the *linear formula was the first suggested*, and is indeed the one which at first thought seems the most plausible:

$$\eta = l + \alpha n.$$

η = the viscosity (in terms of $\eta_{(\text{pure water})} = 1$);
α = constant for the solute in question; n = concentration.

This was found, however, to agree very poorly with the facts; and the so-called *exponential formula* was introduced by Arrhenius. This was found by its originator,[2] as well as by Rehyer,[3] and Wagner,[4] to hold approximately for solutions of electrolytes within rather narrow limits of concentration.

$$\eta = A^x,$$

where η is the viscosity as in the first formula, A is a constant depending on the particular solution, and x is the concentration.

[1] Hagenbach: Pogg. *Ann.*, **109**, 385 (1860).
[2] *Ztschr. phys. Chem.*, **1**, 285 (1887).
[3] *Ibid.*, **2**, 744 (1888).
[4] *Ibid.*, **4**, 31 (1890).

Rudorf,[1] 1903, discusses both of these formulae. He finds that for acetic acid over a wide range of concentration the linear holds better than the exponential formula; and he concludes that the linear formula is the one to be *à priori* expected in case that no polymerization or association of solvent with solute occurs. Reasoning from this assumption, he, in a measure quantitatively, accounts for the deviation from the linear formula in the case of non-electrolytes. Neither of these formulae, however, have a theoretical foundation. Hagenbach,[2] in his deduction of the relation between the coëfficient of viscosity and the flow through capillary tubes, assumes the liquid in the tube to be made up of concentric hollow cylindrical layers, each flowing at a different speed than that next inside or outside, and none of these layers mixing.[3] The layer in contact with the glass wall has the velocity zero; and the core in the middle has the maximum velocity. The viscosity is due to the frictional resistance of these layers moving against each other. A formula derived from the number and kind of molecules in the liquid surface (assuming two given molecules always to offer the same resistance to flow past each other) is complicated and its application is difficult, even to the simplest cases. For a purely physical solution of a single solute, such a formula would contain two arbitrary constants. Polymerization, association of solvent with solute, and electrolytic dissociation influence the kind and number of molecules, and, therefore, the viscosity, in a solution. The extent to which these phenomena take place is, in most cases, not even approximately known. The application of such a theoretically derived formula is manifestly impossible to the solutions used in this research. It was, however, found that the linear formula represented approximately the behavior of all of our solutions used, except at points where definite molecular changes took place. To the viscosity as ordinarily expressed, however, was applied a correction which seems to possess certain advantages.

V. CORRECTION APPLIED TO THE VISCOSITY VALUE.

The viscosity of solutions is most commonly found from the time of flow of a definite volume through a capillary tube under

[1] *Ztschr. phys. Chem.*, **34**, 257 (1903).

[2] Hagenbach: *Loc. cit.*

[3] That this assumption is justified for straight tubes of even bore and smooth interior, and for moderate velocities, see Bovey's "Hydraulics."

the pressure caused by the difference in level of the free surfaces of the bodies of the liquid which the capillary connects. The viscosity is then given by the ratio of the time of flow for the solution to the time of flow for the same volume of pure water, multiplied by the specific gravity of the solution. This leaves out of consideration, however, the amount of solvent displaced from a given volume by the dissolved substance. In the following tables the figure for the viscosity, as usually calculated, will be designated, in the usual manner, by the letter η. To obtain what we shall call the Corrected Viscosity, we have added to the time of flow of the volume of solution, the time of flow of the amount of pure solvent which has been displaced from the given volume by the dissolved substance. This value we shall designate by the character η'.

Figure 1 represents the bulb of the viscosity apparatus used. For all measurements, the time is found which is required for the volume of liquid between the marks *a* and *b* to flow through the capillary tube *c*, by starting the stopwatch when the surface of the liquid passes the mark *a*, and stopping it as the surface passes *b*. When *a b* is filled with a solution, there is a less amount of solvent in the bulb than were it filled with the pure solvent. Suppose we pour pure solvent upon the top of the solution until the portion of the tube *a d* were filled with it and the amount of pure solvent in the total space *b d* were just such as would, in the pure condition, fill the bulb *a b*. This volume *a d* may be readily calculated from the specific gravity of the liquids. The correction is applied by simply adding the value of the ratio of the volumes *a d*/*a b* to the viscosity as ordinarily calculated. In the case of other solvents than water we have still adhered to the viscosity of water at 25° as unity. Hence, in this case, the ratio *a d*/*a b* must be multiplied by the viscosity of the solvent before being applied as a correction.

Fig. 1.

VI. METHOD.

The experimental method used was exactly that described by Ostwald-Luther.[1] The method of expressing results is modified as explained in the preceding section of this article.

[1] *Physiko-chemische Messungen*, II Auflage (Leipzig, 1902), pp. 259-262.

VII. ACCURACY OF THE LINEAR FORMULA.

The closeness with which the facts agree with this formula was tested for the following substances which were to be used in the investigation: ammonia in water, pyridine in water, water in alcohol. The results obtained by us, which are shown in Tables I, II and III, accord well with those of other observers, but are more extensive for the particular substances in question. In the first column are the concentrations of the solutions expressed in molecules per liter. In the next column is the specific gravity at 25°, referred to that of water at 25° as unity. This temperature is that of all the measurements. The third column contains the actual time of flow of the solution through the apparatus. In the fourth and fifth columns are the viscosity η and the corrected viscosity η'. In the last two columns are the ratios of the increase of the viscosity and of the corrected viscosity, respectively, to that of the concentrations. These ratios are designated by D and D', as follows:

$$D = \frac{\Delta\eta}{\Delta \text{ conc.}} ; D' = \frac{\Delta\eta'}{\Delta \text{ conc.}}.$$

TABLE I.—NH_3 IN WATER, 25°.

Conc.	Sp. gr. 25°/25°.	Time. (Water = 98.8.)	η	η'	D	D'
0.0	.....	....	....	.....	....	....
1.30	0.9900	102.2	1.024	1.0561	0.018	0.043
2.66	0.9797	106.5	1.056	1.1216	0.024	0.048
4.16	0.9688	111.4	1.092	1.1943	0.024	0.048
5.93	0.9559	117.4	1.136	1.2810	0.025	0.049
6.60	0.9515	119.6	1.152	1.3124	0.023	0.047
8.39	0.9393	125.0	1.188	1.3917	0.020	0.044

TABLE II.—PYRIDINE IN WATER, 25°.

0.0.	1.0000	1.000	1.000	....	....
0.530	1.0008	1.104	1.145	0.197	0.274
1.060	1.0016	1.211	1.293	0.203	0.279
1.545	1.0023	1.308	1.428	0.200	0.279
2.538	1.0033	1.536	1.736	0.229	0.310
4.73	1.0046	2.015	2.385	0.219	0.296

TABLE III.—H_2O IN ALCOHOL, 25°.

0.0	0.7876	1.211	1.211	....	....
0.257	0.7891	1.236	1.241	0.099	0.118
0.507	0.7909	1.259	1.268	0.094	0.110
3.445	0.8095	1.509	1.571	0.085	0.103
14.33	0.8591	2.180	2.466	0.062	0.082

With solutions of ammonia up to eightfold molar, it is seen that the value of D' varies but little about a mean which may be taken as 0.047. Therefore the linear formula holds approximately for this substance. For solutions of pyridine in water up to the strength of 4.73-fold molar the rate of increase of viscosity is seen to vary not more than 6 per cent. from a mean value of 0.292 although it passes through a slight maximum. For water in ethyl alcohol, the D'-values diminish steadily and quite appreciably from the outset.

If instead of to a pure solvent, small amounts of ammonia, pyridine, water, etc., be added to *solutions,* there would be two possibilities: The added substances might have a strong affinity for the solute, thus combining with it, and displacing any possible molecules of solvent held in combination with it in the form of *solvate.*[1] Or the added substance might have no affinity for the solute. In the latter case we should expect the same increase in the viscosity of the solution as we have previously found in the case of pure solvent. In the former case the compound of the solute with the added substance would have a viscosity of its own, which would probably be entirely different from that of the sum of the viscosities of the solute and of the added substance in solution separately.

VIII. RESULTS WITH METAL-AMMONIA SALTS.

The condition of the metal-ammonia salts in aqueous solution has been considerably studied, so that much concerning their molecular constitution is known. Numerous investigations upon mixed solutions of silver salts and ammonia by means of freezing-point, pressure of ammonia vapor, partition of ammonia with chloroform, solubility, migration, and electrical potential measurements[2] have shown that for every mol of silver salt 2 mols of ammonia exist in the state of combination, while any surplus ammonia exists in the same form as in a simple aqueous solution. The combined ammonia exists as a part of the complex cation $Ag.2NH_3$.

[1] See note 2, page 1318.

[2] Reychler: *Ber. d. chem. Ges.*, **28**, 555 (1895); Konawalow: *Chem. Centrbl.*, **11**, 659 (1898); Gaus: *Ztschr. anorg. Chem.*, **25**, 236-64 (1900); Dawson and McCrae: *Ztschr. anorg. Chem.*, **26**, 94-103 (1901); Bodländer and Fittig: *Ztschr. phys. Chem.*, **39**, 597 (1901); Whitney and Melcher: This Journal, **25**, 69 (1903).

Similar measurements by Dawson and McCrae[1] on copper-ammonia salts by means of the partition of ammonia between chloroform and aqueous phases gave a molecular ratio of *salt* : *fixed* NH_3, which approached the value *4*.

Work of Bonnsdorf,[2] by the method of Bodländer and Fittig of potential measurements, gave the value of *salt* : *fixed* NH_3 for zinc salts as 3.01-3.13.

It seemed best on account of the definiteness of the constitution of these metal-ammonia salts, to first test upon them the method outlined in the last section.

To silver nitrate in solution was first added ammonia in 1 or 2 drops excess of the amount necessary to redissolve the precipitate of silver oxide which first formed. Thereupon the volume was increased with pure water to make the resulting concentration exactly molar as regards silver salt. The viscosity of this solution was determined, then of solutions varying from it only in the ammonia content. In Table IV are found the results, tabulated in

TABLE IV.—NH_3 IN 1.0 MOLAR $AgNO_3$, 25°.

Conc. NH_3.	Sp. gr. 25°/25°.	Time. (Water = 98.8).	η	η'	D	D'
0.0	1.1390	91.8	1.058	1.089	.....	.....
2.04	1.1195	88.3	1.002	1.087	—0.027	—0.001
2.51	1.1157	90.0	1.016	1.113	+0.030	+0.055
3.56	1.1080	92.7	1.040	1.162	0.022	0.047
5.00	1.0967	96.9	1.076	1.234	0.025	0.050
7.03	1.0818	102.7	1.124	1.333	0.024	0.048

the same manner as in the preceding tables. It is seen from the table that the addition of *2* mols of ammonia to 1 of silver salt produces a decrease in the viscosity. Additions of ammonia beyond *2* mols give almost the same values of D and D' as if added to pure water. This offers a confirmation of the conclusion that *2* molecules of NH_3 in solution are united with one of silver salt, forming a stable complex, and that any further amount of ammonia does not unite with the silver salt in solution.

Similar series of experiments were made upon solutions of copper nitrate, copper sulphate (two concentrations), zinc sulphate, and zinc chloride (two concentrations), the results being given in Tables V, VI, VII and VIII.

[1] *J. Chem. Soc.*, 1900, p. 1239.
[2] *Ber. d. chem. Ges.*, 1903, p. 2322.

TABLE V.—NH_3 IN 0.5 MOLAR $Cu(NO_3)_2$.

0.0	1.0727	107.5	1.167	1.188	....	....
2.02	1.0594	95.9	1.028	1.097	—0.069	—0.045
2.55	1.0550	97.4	1.040	1.122	+0.023	+0.047
3.09	1.0509	98.6	1.049	1.145	0.017	0.043
5.06	1.0353	104.4	1.094	1.239	0.023	0.048
7.08	1.0202	110.9	1.145	1.339	0.025	0.049

TABLE VI.—NH_3 IN 0.5 MOLAR $CuSO_4$.

0.0	1.0791	123.9	1.353	1.354	....	....
2.03	1.0677	110.0	1.189	1.236	—0.081	—0.058
3.04	1.0603	114.6	1.230	1.301	+0.040	+0.065
5.99	1.0379	126.6	1.330	1.472	0.034	0.058

NH_3 IN 1.0 MOLAR $CuSO_4$.

0.0	1.1553	158.9	1.858	1.862	....	....
4.08	1.1312	128.4	1.470	1.568	—0.095	—0.072
4.76	1.1271	131.0	1.494	1.608	+0.035	+0.059
5.53	1.1212	134.4	1.525	1.658	0.040	0.065

TABLE VII.—NH_3 IN 0.505 MOLAR $ZnSO_4$.

0.0	1.0808	124.6	1.363	1.362	....	....
2.47	1.0621	109.7	1.179	1.239	—0.075	—0.050
3.25	1.0562	112.6	1.204	1.283	+0.032	+0.056
6.80	1.0292	127.7	1.330	1.496	0.035	0.060

TABLE VIII.—NH_3 IN 0.5 MOLAR $ZnCl_2$.[1]

1[1]	0.0	1.0601	110.8	1.189	1.197	....	....
2	2.53	1.0412	98.2	1.035	1.105	—0.061	—0.036
3	2.86	1.0396	99.5	1.047	1.124	+0.040	+0.063
4	3.69	1.0323	102.8	1.074	1.173	0.031	0.057
5	4.67	1.0251	106.0	1.100	1.223	0.027	0.051
6	6.96	1.0077	115.1	1.174	1.353	0.032	0.057
7	8.35	0.9989	120.6	1.215	1.426	0.029	0.053

NH_3 IN 0.955 MOLAR $ZnCl_2$.[1]

8[1]	0.0	1.1174	122.3	1.383	1.403	....	....
9[1]	0.0	1.1139	120.8	1.262	1.381	....	....
10	4.51	1.0820	99.9	1.094	1.219	....	....
11	6.68	1.0667	107.9	1.165	1.342	+0 033	0.057
12	10.98	1.0363	127.0	1.332	1.613	0.039	0.063

[1] Solutions of $ZnCl_2$ can not be diluted with pure water without a precipitation of basic salt. To the stock solution for Nos. 1-7 inclusive has been added hydrochloric acid to make 0.024 molar on the final dilution. No. 1 contains a further addition to make 0.045 molar. In Nos. 8-12 inclusive sulphuric acid was used by mistake instead of hydrochloric acid in an amount to make 0.016 molar on dilution. Nos. 8 and 9 contain additional amounts to make 0.079— and 0.030 molar respectively.

The precipitate of basic copper salt redissolved in each case in somewhat less than 4 mols of ammonia to 1 of copper salt, but the first determinations were made on solutions containing fully 4 molecules. A copper-ammonia salt containing but 2 molecules of NH_3 is known to exist, but the more stable complex salt is that containing 4 molecules. In the case of copper nitrate, additions of ammonia in excess of four equivalents give the normal D' values. With copper sulphate, on the other hand, values of D' some little higher than, but still not far removed from, the normal are obtained. This would indicate that ammonia in excess of four equivalents still had some action upon copper sulphate, but that this action was very much more feeble than that of the first 4 mols. Copper ammonium nitrate crystallizes with the composition $Cu(NH_3)_4(NO_3)_2$, while copper ammonium sulphate crystallizes as $Cu(NH_3)_4SO_4.H_2O$. Of the ammonia-free salts, copper nitrate at a low temperature, crystallizes as $Cu(NO_3)_2.6H_2O$, while copper sulphate can, under certain conditions (when mixed with other vitriols), exist as $CuSO_4.7H_2O$.[1] The sulphates then seem to have the power in the solid state of combining with more molecules of H_2O than do the nitrates. This power is most probably due to the negative component, and is also possibly possessed by the SO_4-radical when in the dissolved state. In copper nitrate solution it is shown that only 4 molecules of NH_3 unite with an atom of Cu. In copper sulphate solution further action with ammonia is probably that of the (possibly hydrated) SO_4-radical.

To redissolve the basic zinc salt, which at first precipitates, ammonia considerably in excess of four equivalents is necessary at the dilutions used, although in very concentrated solutions a bare excess is sufficient. Zinc chloride itself forms a basic salt with pure water, so that to the stock solution, which was used for the dilutions, a small amount of acid, as indicated in the tables, was added. This solution, on further dilution with water, again precipitated basic salt, making necessary a slight further addition of acid before determining the viscosity of the non-ammoniacal solutions. The zinc-ammonia salts which crystallize from ammoniacal solutions are $Zn(NH_3)_4Cl_2.H_2O$ and $Zn(NH_3)_4SO_4.4H_2O$.

[1] Dammer: "Anorganische Chemie," Band II, 2.

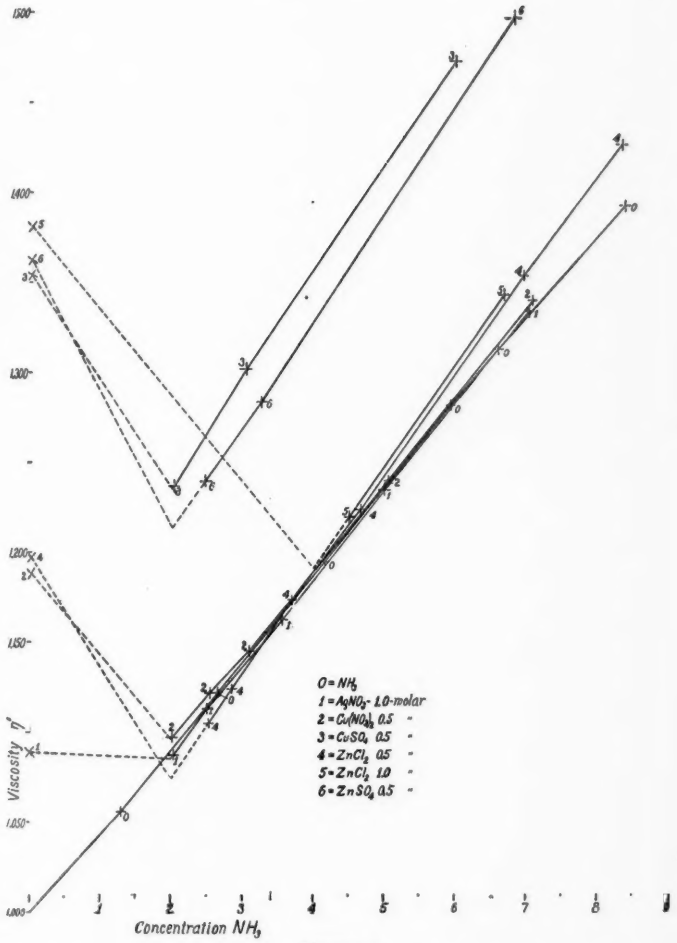

Diagram 1.

$ZnSO_4.5NH_3$ can be obtained by leading ammonia gas over dry $ZnSO_4$, but this complex is readily decomposed by water.[1] The D' values for ammonia with zinc chloride and zinc sulphate are a little above the normal, which indicates, as in the case of copper sulphate, that after the formation of the fairly stable metal-

[1] Dammer: "Anorganische Chemie," Band II, 2.

ammonia complex ($Zn.4NH_3$), there is some slight further tendency for ammonia to react with the salt and indeed most probably with the negative component.

The foregoing results are represented graphically in Diagram 1, where abscissae represent concentrations of NH_3 and ordinates the values of η'. For the nitrates the values of η' fall off sharply to the points where ammonia, sufficient to give a clear solution, is present; from there on the curves for the nitrates coincide almost exactly with that for ammonia and pure water. For zinc chloride at two different dilutions the same is nearly true; but for the sulphates, although the addition of the first 4 molecules of ammonia causes a great decrease in the values of η', the entire curve is very much above, although its latter portion runs in about the same direction as, the curve for ammonia in pure water. If curves for the uncorrected viscosity, η, be drawn, much the same characteristics are shown in that the addition of 2 or 4 molecules, respectively, of ammonia causes a great drop, and that further additions of ammonia cause a steady rise. But with the uncorrected viscosity the curves for the nitrates and chlorides investigated are no longer nearly coincident with each other and with that for ammonia and pure water.

Some rather rough experiments with pyridine and copper nitrate were tried with the results in the following table:

PYRIDINE IN 0.4 MOLAR $Cu(NO_3)_2$, 25°.

Conc.	Pyridine.	Sp. gr.	η	η	D	D'
....	0.0	1.058	1.140	1.156	....	....
....	1.84	1.062	1.626	1.784	+0.26	+0.34
....	2.03	1.063	1.697	1.870	0.37	0.45

Apparently pyridine forms a complex with the copper salt in exactly the same manner as does ammonia, for the basic copper salt, precipitated by the first addition, dissolves when somewhat in excess of four equivalents of pyridine have been added, and the color of the resulting solution is identical with that of the copper-ammonia salts. The D values, however, show a large increase in viscosity from the simple salt to the pyridine complex salt. This is what would be expected, for addition of such large molecules as pyridine, even though they might displace water molecules, could hardly otherwise than greatly increase the viscosity of the copper salt molecules.

Dissolved molecules, if in a state of purely physical solution, may be supposed to offer friction according to their nature; and the relation between that friction and the molecular weight and constitution of the molecules is probably of the same order of magnitude whether we are dealing with the molecules of pure liquids or of dissolved substances. To place clearly before us the effect of molecular weight and constitution upon viscosity, the values for a number of typical liquids have been taken from Landolt and Börnstein's tables. The values are all for 20° (interpolated where necessary); they are expressed in the absolute measure, and in some cases they are the average of values by different observers.

TABLE IX.—VISCOSITY OF PURE LIQUIDS, 20°.

(Taken from Landolt and Börnstein's Tables.)

Substance.	Molecular weight.	Viscosity.
Ethyl ether	74	0.0026
Carbon bisulphide	76	0.0037
Propyl chloride	78	0.0036
Ethyl bromide	109	0.0038
Chloroform	120	0.0057
Propyl bromide	123	0.0055
Carbon tetrachloride	154	0.0102
Ethyl iodide	156	0.0059
Propyl iodide	170	0.0076
Ethylene bromide	186	0.017
Methyl propionate	88	0.0047
Ethyl acetate	88	0.0046
Propyl formate	88	0.0057
Isopropyl formate	88	0.0052
Methyl butyrate	102	0.0059
Ethyl propionate	102	0.0055
Propyl acetate	102	0.0061
Isopropyl acetate	102	0.0054
Butyl formate	102	0.0070
Benzene	78	0.0065
Toluene	92	0.0060
Xylene	106	0.0067
Water	18	0.0102
Methyl alcohol	32	0.0062
Ethyl "	46	0.012
Propyl "	60	0.023
Butyl "	74	0.013
Amyl "	88	0.037

TABLE IX.—(*Continued.*)

Substance.	Molecular weight.	Viscosity.
Formic acid	46	0.019
Acetic "	60	0.013
Propionic acid	74	0.011
Butyric acid	88	0.016
Valerianic acid	102	0.022

For the first group of liquids the general statement may be made that the viscosity is greater, the greater the molecular weight, although the two quantities are far from being exactly proportional.

In the next two groups is shown the effect of structure in series of isomeric compounds. As a general rule, it may be stated that the more symmetrical the structure the lower the viscosity.

In the last two groups in the table are some of the substances which, in the liquid form, we have good reason to believe do not exist as the simple molecules indicated by their chemical formulae, but as polymers of these. It is noticed, first, that the viscosities of bodies in the latter groups are much higher than of those of the same molecular weight in the first four groups; and second, that there is here much less regularity in increase of viscosity with the increase of the molecular weight corresponding to the simple formulae.

Let us try to interpret the behavior of the metal-ammonia salts in the light of our knowledge of pure liquids. Addition of 2 and 4 mols respectively of ammonia to solutions of silver, copper and zinc salts decreases very greatly the viscosity. Probably the degree of ionization of the metal-ammonia salts is slightly greater than that of the plain metal salts. This will, however, hardly account for the large decrease in viscosity, for Wagner[1] found, without taking ionization into account, that the viscosity of salts is, in general, very nearly equal to the sum of definite values assigned to each of the metallic and acidic atoms or radicals respectively; Rehyer[1] further found that the sodium salts (dissociated) of various weak organic acids possessed, in normal solutions, viscosities higher, by values ranging from 0.18 to 0.41 than those of the corresponding undissociated acids. Furthermore substitution of the dissociated *H*-ion by *Na*-ion in normal solu-

[1] *Loc. cit.*

tions of strong mineral acids increased the viscosity only by the almost constant amount 0.035. This would show that weak acids would, if dissociated, possess specific vicosities greater by values from 0.15 to 0.38. This would indicate that the increased dissociation is not the cause of the decreased viscosity of the ammonia-metal salts. Also it furnishes another argument against the Electrostriction hypothesis of negative viscosity. The only way then open to account for the decreased viscosity seems to be a decrease in size or an increase in symmetry of the salt molecules, or more especially of the positive ions of the salts (since ammonia is shown by migration experiments to form a part of that ion). If the positive ion consists solely of a metallic atom bearing an electric charge, combination with ammonia molecules cannot de-

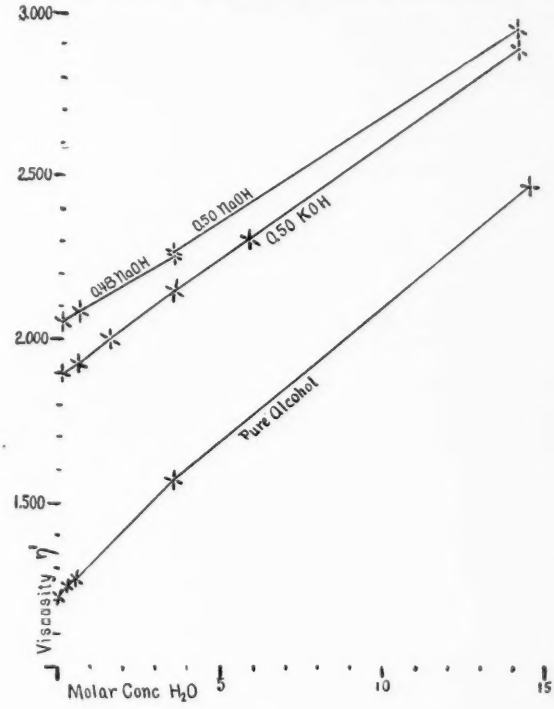

Diagram 2.

crease its mass and it is not easy to imagine that it can increase its symmetry. The only explanation then seems to be that metal ions in solution are hydrated; the hydrate-water is replaced by ammonia, which forms with the ion a more stable complex and one of lesser mass, or greater symmetry, or both. It will be seen that this explanation of the lowering of viscosity of a metal salt solution by addition of ammonia is similar to the one offered earlier in this paper, of negative viscosity.

This work has shown that where definite and fairly stable complexes are formed in solution their presence can, at least in certain cases, be clearly and quite conveniently demonstrated by means of viscosity measurements.

An attempt was now made, working in alcoholic solution, to show the existence of complexes of metal salt with water similar to those of metal salt with ammonia in aqueous solution. While the indications of these experiments are far less definite than of those just described, the data are nevertheless of some interest to present.

IX. THE EFFECT OF ADDITIONS OF WATER TO SOLUTIONS IN ABSOLUTE ETHYL ALCOHOL.

Series of viscosity measurements were made, similar, in every respect, to those with the metal-ammonia salts. In place of metal salts the hydroxides of lithium, sodium and potassium, and anhydrous cupric chloride were used. Instead of water absolute ethyl alcohol was the solvent, and instead of ammonia, water was the substance added in varying amounts.

The solutions were prepared by dissolving metallic sodium, metallic potassium, lithium hydroxide, and anhydrous cupric chloride respectively in absolute alcohol. For each experiment a definite amount of the proper solution was taken, the desired amount of water added, and the whole made up to a fixed volume with absolute alcohol.

The results for sodium and potassium hydroxides are found in Tables X and XI. For the first additions of water to pure alcohol the value of D' may be taken as approximately 0.11—it decreases with increasing concentrations, according to Table III. On addition of water to alcoholic sodium hydroxide this value is found to be only 0.06 and on addition of water to alcoholic potassium hydroxide 0.07. As the concentration of the water increases, the

values of the ratio, particularly in the case of the potassium hydroxide solution, are more nearly the same as those for the same amount of water added to pure alcohol. These relations are shown graphically in Diagram 2. That the curves for the solutions do not run parallel with that for pure alcohol, in other words, that the D' value is altered by the dissolved hydroxide, shows that there has been some interaction of the added substances with the solute. That the curve for sodium hydroxide is inclined more than that for potassium hydroxide towards the curve of pure alcohol shows, as well as does the greater change in the D' value, that more of the added water is acted upon by the sodium hydroxide.

TABLE X.—H_2O TO 0.5 MOLAR NaOH IN ETHYL ALCOHOL.

	Concentration.	Sp. gr. 25°/25°.	η	η'	D	D'
1	$NaOC_2H_5$, 0.48, ...	0.8085	2.0419	2.060	....	....
2	NaOH, 0.48: H_2O, 0.020	0.8113	2.0565	2.050	0.029	....
3	NaOH, 0.48: H_2O, 0.510	0.8142	2.0777	2.081	0.043	0.063
4	NaOH, 0.48: H_2O, 3.435	0.8302	2.1911	2.252	0.039	0.058
5	$NaOC_2H_5$, 0.050, ...	0.8084	2.0467	2.068	....	....
	NaOH, 0.50: H_2O, 3.435	.....	2.1959	2.260	(extrapolated from 5, 4 and 1)	
6	NaOH, 0.50: H_2O, 13.92	0.8822	2.6726	2.944	0.045	0.065
7	NaOH, 0.50: H_2O, 20.19	0.9103	2.9465	3.348	0.044	0.064

TABLE XI.—H_2O TO 0.5 MOLAR KOH IN ETHYL ALCOHOL.

KOC_2H_5, 0.50, ...	0.8130	1.8677	1.893	....	....
KOH, 0.50: H_2O, 0.01	0.8159	1.8930	1.893	0.050	....
KOH, 0.50: H_2O, 0.50	0.8187	1.9182	1.927	0.051	0.069
KOH, 0.50: H_2O, 1.47	0.8245	1.9740	2.001	0.058	0.076
KOH, 0.50: H_2O, 3.44	0.8354	2.0837	2.149	0.056	0.075
KOH, 0.50: H_2O, 5.71	0.8473	2.1965	2.306	0.050	0.070
KOH, 0.50: H_2O, 13.93	0.8869	2.6060	2.883	0.050	0.070

TABLE XII.—H_2O TO 0.162 MOLAR LiOH IN ETHYL ALCOHOL.

LiOH, 0.162, ...	0.7961	1.5216	1.5145	....	....
LiOH, 0.162: H_2O, 0.358	0.7984	1.5543	1.5537	0.091	0.109
LiOH, 0.162: H_2O, 0.664	0.8002	1.5797	1.5848	0.083	0.102
LiOH, 0.162: H_2O, 1.32	0.8043	1.6330	1.6499	0.081	0.099

TABLE XIII.—H_2O TO 0.163 MOLAR NaOH IN ETHYL ALCOHOL.

$NaOC_2H_5$, 0.163, ...	0.7949	1.4614	1.4682	....	....
NaOH, 0.163: H_2O, 0.006	0.7961	1.4769	1.4740	0.091	....
NaOH, 0.163: H_2O, 0.210	0.7975	1.4926	1.4932	0.077	0.094
NaOH, 0.163: H_2O, 0.662	0.8006	1.5351	1.5434	0.094	0.111
NaOH, 0.163: H_2O, 1.33	0.8046	1.5857	1.6065	0.076	0.094

Owing to the small solubility of lithium hydroxide in alcohol only a 0.270 molar (almost saturated at 25°) solution could be prepared; 15 cc. of this were in each experiment diluted to 25 cc., thus giving an 0.162 molar solution. To compare with this series, a series of measurements was also made with the same strength of sodium hydroxide solution. From the results given in Tables XII and XIII it is seen that with these weak solutions there is but little change of the D' value. Thus, from a difference in the amount of the decrease it is not possible to say that either one or the other hydroxide has a greater action upon water. It is, however, seen that lithium hydroxide in alcohol has a higher viscosity than sodium hydroxide. The viscosities of the alkali hydroxides in alcohol increase from potassium to lithium, as well as do the viscosities of the salts of the alkalies in water.

In Table XIV and in Diagram 3 is shown the behavior of all mixtures of alcohol and water. My own values for these mixtures are given, since values at the concentrations and the temperature desired were not to be found. The form of the curve is, however, identical to that found by others. Small additions of water to alcohol or of alcohol to water cause a great increase of the viscosity. As shown in the curve, the maximum lies about at a point corresponding to a composition of $1C_2H_5OH + 3H_2O$. This might indicate, as has already been suggested by Graham,[1] by Thorpe and Rodgers,[2] and others, a definite though very unstable compound of the formula $C_2H_5OH.3H_2O$. It is otherwise hard to explain the great increase of the viscosity above the sum of the viscosities of the individual components. In cases where there is less probability of a compound being formed no such increase is observed. For example, the viscosity curves for mixtures of non-polymerizing liquids, such as benzene and toluene, benzene and carbon bisulphide, carbon tetrachloride and chloroform, etc.,[3] are either nearly straight lines or are convex downward.

Water added to alcoholic sodium hydroxide or potassium hydroxide can combine, first, with alcohol to form the hypothetical $(C_2H_5OH.3H_2O)$. If only this reaction took place, however, D' would equal 0.11. Secondly, it can combine with ROH, possibly displacing any alcohol which may exist in a compound of

[1] *Phil. Mag.* (4), **24**, (1862).
[2] *J. Chem. Soc.*, **71**, 360 (1897).
[3] Linebarger: *Am. J. Sci.*, IV., **2**, 331 (1896); also Thorpe and Rodgers: *Loc. cit.*

the form $ROH.nC_2H_5OH$. At all events if combination with water does increase the friction of the ROH-complex above that of the *ROH-alcohol*-complex, such increase, as is shown by the results, is less than that which would have been caused by the formation of the compound $C_2H_5OH.mH_2O$. Were a definite hydrate $ROH.lH_2O$ formed of a stability comparable to that of the metal-ammonia compounds, we should expect to get a curve like those for the latter, with a sudden change in direction at the point where just l water molecules have been added. We have, however, rather an equilibrium:

$$\mathrm{ROH \cdot } n\mathrm{C_2H_6OH} + \frac{l}{m}\,(\mathrm{C_2H_5OH}.m\mathrm{H_2O}) \rightleftharpoons$$

$$\mathrm{ROH \cdot } l\mathrm{H_2O} + \left(n + \frac{l}{m}\right)\mathrm{C_2H_5OH},$$

in which the attraction of ROH for alcohol is so great (shown by its heat of solution in alcohol) that the reaction does not proceed by any means until one of the substances upon the left-hand side is exhausted. All we can expect then, upon successive additions of water, is to get a gradual displacement of the equilibrium towards the right which would result in giving a viscosity curve more or less inclined to that of water and pure alcohol.

Sodium hydroxide in alcohol has a greater viscosity than potassium hydroxide. If we account for this in the same way as in the case of aqueous solutions, we should conclude that the *Na-alcohol*-complex had a greater mass or was less symmetrically constituted than the *K-alcohol*-complex. Sodium hydroxide, from its greater effect upon the values of D', appears to have a greater tendency than has potassium hydroxide to combine with water. This is not at variance with the suggestion that the sodium ion, with its water of hydration, has a greater mass than the potassium ion.

It might be claimed that variations from the normal D value were caused by changes in the degree of electrolytic dissociation produced by the additions of water. Small amounts of water, however, do not materially change the nature of the solvent. Hence, if there are marked changes in the dissociation, it would seem that the dissociation itself must be caused by the chemical combination of electrically neutral molecules with the solute.

X. COPPER CHLORIDE IN MIXTURES OF ALCOHOL AND WATER.

The stock solution of copper chloride was prepared by dissolving dehydrated copper chloride in absolute alcohol. Here a very considerable evolution of heat was noticed with the first additions of alcohol, and there was formed a deep greenish brown solid mass. This dissolved in a further small addition of alcohol with no further evolution of heat. To this was added a small amount of an alcoholic solution of dry hydrochloric acid. The solution was now made up with absolute alcohol to give a concentration of 2 mols of copper chloride and 0.065 mol of hydrochloric acid.

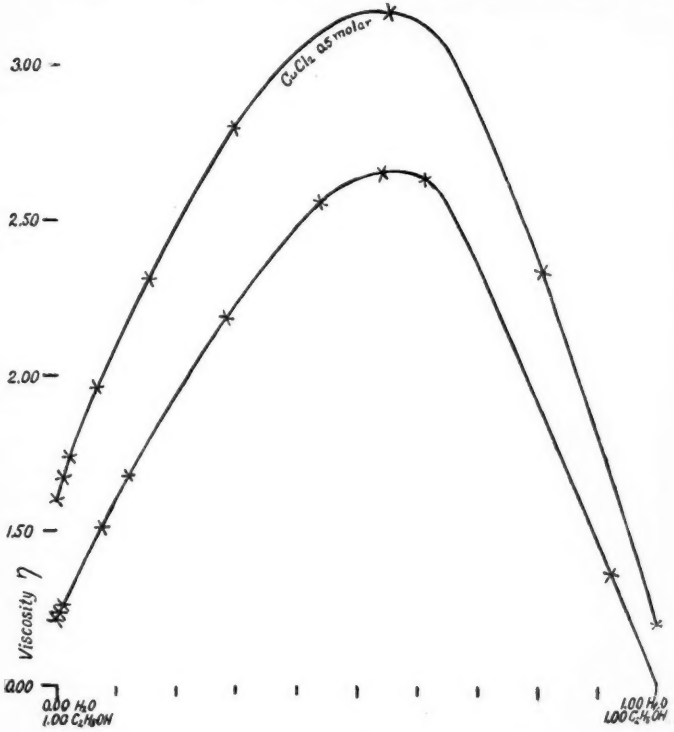

Diagram 3.

The small amount of acid was put in the solution for the purpose of preventing precipitation of any basic salt upon dilution. For three of the mixtures this was found to be not quite sufficient to

prevent a slight visible turbidity. Measurements were, however, made in these cases without further addition of acid and with additions sufficient to entirely remove the turbidity. It was found that these small additions of hydrochloric acid did not greatly affect the viscosity.

TABLE XIV.—H_2O IN ETHYL ALCOHOL.

Parts water. / Parts water + alcohol.	Concentration water in molecules.	η
0.0	0.0	1.211
0.006	0.257	1.236
0.012	0.507	1.259
0.077	3.45	1.509
0.120	5.50	1.675
0.281 ($C_2H_5OH.H_2O$)	13.46	2.180
0.439 ($C_2H_5OH.2H_2O$)	21.8	2.551
0.540 ($C_2H_5OH.3H_2O$)	27.6	2.650
0.610 ($C_2H_5OH.4H_2O$)	31.6	2.628
0.920	50.4	1.352
1.000	55.4	1.000

TABLE XV.—H_2O AND 0.5 $CuCl_2$ IN ETHYL ALCOHOL.

	Parts water. / Parts water + alcohol.	Concentration water in molecules.	Concentration hydrochloric acid in molecules.	Sp. gr. $25°/25°$.	η	D
1	0.00	0.0	0.016	0.8455	1.599	....
2	0.0115	0.50	0.016	0.8488	1.669	0.140
3	0.0229	1.00	0.016	0 8521	1.737	0.136
4	0.0665	2.94	0.016	0.8644	1.958	0.114
5	0.152	6.89	0.016	0.8857	2.308	0.089
6	0.291	13.8	0.016	0.9193	2.794	0.070
7	0.546	27.6	0.016	0.9793	3.163	0.027
7*b*	0.546	27.6	0.15	0.9813	3.168	....
8	0.804	42.8	0.016	1.0273	2.323	....
8*b*	0.804	42.8	0.24	1.0303	2.304	....
9	1.00	51.2	0.08	1.0582	1.193	....

The experimental results are given in Table XV, and in Diagram 3 are shown graphically the viscosities for mixtures of alcohol and water, alone, and with 0.5 molar copper chloride. Increasing from either pure solvent the curve mounts more steeply in presence of copper chloride, that is, presence of copper chloride causes an increase in the D value rather than a decrease, as in previous instances. The cause of this phenomenon is doubtless much the same as that of the phenomenon found by Jones and

Lindsay,[1] that the conductivity of certain salts in mixtures of water with methyl, ethyl and propyl alcohols usually shows a strong minimum. A maximum of viscosity corresponds closely to a minimum of conductivity and would seem to us to be caused by a maximum amount of polymerization or of association of solute and solvent, rather than by a mutual lessening of the polymerization of each simple solvent.

SUMMARY.

The relationship between migration velocity and the viscosity of ions in solution is discussed.

Negative viscosity is discussed and an attempt is made to account for it on the ground of the hydration of *solvation*[2] of the dissolved substance.

The viscosity of solutions as ordinarily represented takes into account only the given volume of liquid which contains the dissolved substance, applying thus to varying amounts of the solvent. A correction is used which, to a certain extent, fulfils the purpose of having the figure for each dilution always refer to the same amount of solvent.

Measurements are given for various additions of ammonia to some of the metal salts which give soluble metal-ammonia compounds. Sufficent ammonia to form the complex compounds in each case causes a large decrease in viscosity; further additions of ammonia cause nearly the same increase in viscosity as if made to pure water. The composition of the complex existing in solution can be inferred from the form of the viscosity curve. The conclusions from this method agree with the well-established facts regarding these solutions. An inspection of the curves of the corrected viscosities shows that beyond the point of re-solution of the basic salt the curves for silver nitrate, copper nitrate, zinc chloride and pure water almost coincide, while the curves of the sulphates of zinc and copper lie considerably above, but run roughly in the same direction as the former. If the curves are drawn for the uncorrected viscosity, the same conclusions regarding composition are made evident, but the latter striking peculiarity is not seen.

The decrease of viscosity with the addition of ammonia to metal salt solutions is compared with the negative viscosity of certain solutions and both seem to find a reasonable explanation in the *Hydrate* or *Solvate Theory* of solution.

[1] *Am. Chem. J.*, **28**, 329 (1902).
[2] See note 2, page 1318

A few series of determinations with additions of water to solutions in ethyl alcohol were made. No very definite conclusions are drawn from them, yet they support, to a certain extent, the suggestion made that the slower rate of migration and the higher viscosities of the ions of the alkali metal, lowest in atomic weight, are due to a greater tendency to combine with molecules of solvent. A maximum of *increase* in viscosity for copper chloride in mixtures of ethyl alcohol and water corresponds with the minimum in conductivity, observed by Jones and Lindsay, in similar solutions, both perhaps being due to a maximum formation of highly associated molecules.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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THE MIGRATION OF COLLOIDS.

BY W. R. WHITNEY AND J. C. BLAKE.

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I. PREPARATION AND DIALYSIS OF COLLOIDAL GOLD SOLUTIONS.

MOST of the work described in this paper was done with red colloidal gold, prepared by pouring an ethereal solution of gold chloride (dried at 160° to 170°) into water saturated with ether and acetylene gas.[1] The reduction was completed by the passage of more acetylene, but an excess of this reagent is to be avoided, since otherwise the presence of the supernatant layer of ether has a tendency to turn the red gold blue at the surface between the two liquids, thus often giving a purple or violet tint to the resulting solution. Such red, purple or violet solutions were then dialyzed in tubing of parchmentized paper, so as to remove the hydrochloric acid formed by the reaction. The progress of the purification was followed by measuring the conductivity of the liquid within the dialyzer. The dialysis was carried out by surrounding the parchment tube first with ten times its volume of ordinary distilled water, frequently renewing this until the electrolyte was mainly removed, and then replacing it by conductivity water (of conductivity 1.5×10^{-6} reciprocal ohms). The specific conductivities (κ) (in reciprocal ohms $\times 10^{-6}$) of the four gold

[1] Blake: *Am. J. Sci.*, **16**, 381 (1903).

solutions used in our migration experiments after the dialysis had been continued for different periods of time, expressed in days, are shown in Table I.

TABLE I.—CONDUCTIVITY OF COLLOIDAL GOLD SOLUTIONS DURING DIALYSIS.

Solution No. 1—red. Final concentration 300 mg. per liter.		Solution No. 2—red, turbid. Final concentration 476 mg. per liter.		Solution No. 3—violet. Final concentration 320 mg. per liter.		Solution No. 4—red. Final concentration 146 mg. per liter.	
Time intervals.	$\kappa \times 10^6$.	Time intervals.	$\kappa \times 10^6$.	Time intervals.	$\kappa \times 10^6$.	Time intervals.	$\kappa \times 10^6$.
3.5	...	7	10.3	0	1690.0	0	1070.0
0.5	12.7	2	8.5	1	206.0	0.25[1]	107.0
4.0	12.3	.	..	0.3	57.7	2	36.6
2.0	...	.	..	2	20.8	1	20.5
3.0	11.2	.	..	1	14.0	1	12.7
2.0	14.7	.	..	7	11.7	.	...
1.0	14.4	.	..	5	9.7	.	...
..	...	.	..	4	11.3	.	...
..	...	.	..	1	9.7	.	...

[1] Running tap water.

It is evident that most of the conducting substance (the hydrochloric acid) is removed within four or five days and that after that time the conductivity remains nearly constant at a value six to eight times that of the conductivity water. It was also proved that the conductivity of the water outside the dialyzer finally remained nearly constant; thus at the end of the experiments with solution No. 3, recorded in the table, the dialyzing tube was placed in about ten times its volume of water having a conductivity of 1.75×10^{-6}; at the end of twenty-four hours the conductivity of this water had increased only to 1.97×10^{-6}, a change which might well have arisen through contamination from the air and sides of the jar. It seems, therefore, justifiable to conclude that the solution contains no more free electrolyte than the outside water, and that most of its conductivity arises from the migration of electric charges on or intimately associated with the gold particles themselves.

Incidentally it is of interest to mention that, as previously observed by Faraday,[1] on long standing the blue gold present in the purple and violet solutions is taken up by fungus growths and that it settles out, leaving the solutions pure red. Thus, after a month gold solution No. 4 had changed from purplish red to

[1] Faraday: *Phil. Trans.*, 1857, p. 159.

pure red and gold solution No. 3 from violet to purple, which later became red. It may also be noted that a mass of coagulated blue gold was changed to a red colloidal solution by contact with fairly strong ammonium hydroxide for two or three weeks.

II. PREVIOUS WORK ON THE MIGRATION OF COLLOIDS.

Until quite recently most of the work along this line was confined to the migration of mechanically prepared suspensions of visible particles and was connected with investigations on electrical endosmose. All of this earlier work is well summarized in the text-books.[1] It was found that all particles suspended in water migrated toward the anode; except that Quincke[2] states that when the potential gradient was low enough a reversal in their direction took place along the walls of the tube owing to the current of water there flowing toward the cathode. His experiments[3] with lycopodium particles suspended in water show that their rate of migration is directly proportional to the potential gradient, though this conclusion is not definitely drawn by the author. The actual rate of migration of these particles is readily calculated from his data to be 0.00025 cm. per second for a potential gradient of 1 volt per centimeter.

The first extended investigation of the behavior of colloids towards the electric current was carried out by Picton and Linder.[4] They found that various colloids contained in a vertical tube migrated downwards with a sharp surface of demarcation, when a potential difference of suitable sign, which varied with the nature of the colloid, was applied. This boundary could be migrated upwards by reversing the current, but the colloid could not be raised completely from the lower electrode except in the case of dilute solutions containing very fine particles, owing to the effect of gravity. Out of sixteen colloids tested they found that eleven migrated toward the anode and five toward the cathode. They state further that in general the direction of migration is in agreement with the acidic or basic character of the colloid. They noticed, also, that with certain colloids after prolonged action of the current the surface of demarcation which had been steadily moving downward reversed its direction and began to move up-

[1] See Wiedemann's "Electricität," Vol. II, p. 166 (1883); Lehmann's "Molecularphysik," Vol. I, p. 830 (1888).

[2] Pogg. *Ann.*, **113**, 569, 582 (1861).

[3] *Ibid.*, **113**, 580.

[4] *J. Chem. Soc.*, **71**, 568 (1897).

wards without any change being made in the electrical connections. This phenomenon is generally referred to as the "reverse movement."

These results, so far as the direction of migration is concerned, were confirmed and extended by Spring[1] and by Lottermoser.[2] From these agreeing determinations one may conclude that aqueous colloidal solutions of the noble metals, of metallic sulphides and of mechanically prepared suspensions contain negatively charged particles, whereas basic hydroxides (iron, aluminum, thorium, etc.), together with some dyestuffs, contain positively charged particles.

In 1899 Hardy[3] clearly pointed out the fact that the direction of migration of egg-albumen depends on the nature of the solution, the colloid going to the anode in alkaline solution and to the cathode in acid solution. When the solution was exactly neutral the colloid coagulated. Hardy also observed a "reverse movement," which he attributed to the action of the electrolytes accumulated around the poles by the action of the current. Later he reproduced all the same phenomena with globulin,[4] and determined its rate of migration to be equal to that of the calcium ion.

A pronounced reverse movement was also obtained by one of us[5] with red colloidal gold.

That most colloids are coagulated and precipitated by the passage of the electric current is well established.[6] Zsigmondy found that his red gold solution was simultaneously turned blue. Spring showed, further, that Röntgen rays, the brush discharge, connection with one pole of a Holtz machine, the alternating current from an induction coil and a single pole of an electric circuit are without apparent effect, thus greatly distinguishing these preparations from suspensions of particles in gases.

In 1898 Coehn,[7] extending the idea of contact electrification previously applied to electrical endosmose, showed that in all the cases tested, with one exception, the electricity generated upon either liquid or solid substances by contact, as determined by the

[1] *Rec. trav. chim. Pays-Bas.*, **19**, 220 (1900).

[2] "Ueber anorganische Colloide," p. 76 (1901), Stuttgart.

[3] *Jour. physiol.*, **24**, 292 (1899).

[4] *Ibid.*, **29**, XXVI (1903).

[5] Blake: *Am. J. Sci.*, **16**, 433 (1903).

[6] Zsigmondy: *Ann. Chem.* (Liebig), **301**, 36 (1898); Bredig's "Anorganische Fermente," 1901, p. 28 (Leipsic); Spring: *Loc. cit.*, p. 209.

[7] *Wied. Ann.*, **64**, 217.

direction of their migration, was always such that the substance having the higher dielectric constant took the positive charge. The dielectric constant of water is the highest known; hence substances suspended in water should be negatively charged. This is generally the case with mechanical suspensions, but it is evident that this theory does not apply to the colloidal solutions used by Picton and Linder, and by Hardy.

The recent work of Billitzer[1] offers a possible explanation of this variance between the ideas based on chemical conceptions and those based on "contact electricity" by applying the theory of the electrical double-layer. Billitzer maintains that colloidal particles of the noble metals act as an oxygen electrode, or after treatment with hydrogen as a hydrogen electrode, toward the surrounding medium, whereas silver acts as a silver electrode. From a consideration of the concentration of the active substance in the particles and of the corresponding ions in the liquid, the potential difference between them may be predicted, and consequently the direction of migration. Conversely, at the concentration at which the direction of migration reverses (Hardy's "iso-electric" point), the potential of the metal toward the liquid is zero. This fact was made the basis of a new method for determining absolute potentials.

In this connection it is interesting to note that Perrin[2] has found that the direction of electrical endosmose through semi-permeable plugs, made of different substances, depends on the acid or basic nature both of the plug and of the liquid. Basic plugs in pure or acidified water cause electrical endosmose to the anode; chemically neutral plugs also have this effect in acid solution, but cause the water to flow to the cathode in alkaline solution.

An interesting experiment of Lehmann's[3] should not be omitted in this connection. He found that when a difference of potential was maintained between electrodes immersed in solidified gelatine containing suspended particles, a dark region gradually extended from the anode and a light one from the cathode. Where the boundaries of these regions met, the suspended particles were precipitated and the gelatine melted. It would seem that the extension of the light region was the primary effect of migration,

[1] *Wied. Ann.*, **11**, 902 (1903).
[2] *Compt. Rend.*, **136**, 1441 (1903).
[3] *Wied. Ann.*, **52**, 455 (1894); *Ztschr. phys. Chem.*, **14**, 301.

and that of the dark region was the "reverse movement." This experiment will be referred to again.[1]

Picton and Linder[2] have further found that two different colloids which have the property of migrating in opposite directions precipitate or partially coagulate each other when their solutions are mixed. Biltz[3] has furnished further evidence of this phenomenon. It is evident that even in a single colloidal solution, after the reverse movement has set in, oppositely charged particles must be present and coagulation might be expected to ensue. That in the case of colloidal gold the particles brought together by the reverse movement become neutral and cease to migrate, but without apparent coagulation, has been shown by an experiment made by one of us.[4]

III. APPARATUS AND METHOD USED IN THE MIGRATION EXPERIMENTS.

The apparatus used in these experiments consisted of vertical glass tubes 2.45 or 2.75 cm. in diameter and 30 to 50 cm. in length, closed at both ends with goldbeaters' skin. Holes were blown in the sides of the tube at varous heights to enable the portions of liquid above them to be separately withdrawn at the end of the experiment by means of a pipette, for the purpose of determining their conductivity; during the experiment these holes were closed with rubber bands. The lower end of the tube was placed in an open vessel usually containing 100 cc. of water. Just beneath and in contact with the membrane at the foot of the tube was placed an electrode consisting either of a straight platinum wire or of a platinum ring. Over the top of the tube was placed a slightly wider tube held in place by a rubber band. Into this upper tube a similar electrode was introduced in contact with the membrane, and it was filled with 50 cc. of water. In some cases a slow current of conductivity water was passed through

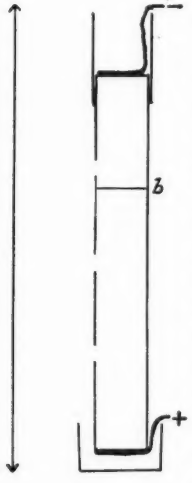

Fig. 1.

[1] See also Bechhold : *Ztschr. phys. Chem.*, **48**, 422 (1904).
[2] *Op. cit.*, **71**, 572. Compare also Spring : *Op. cit.*, **19**, 222.
[3] *Ber. d. chem. Ges.*, **37**, 1095, 1766 (1904).
[4] Blake : *Loc. cit.*

the compartments surrounding the two electrodes. In the vertical tube itself was usually placed one of the completely dialyzed gold solutions already described. This was always allowed to stand in the tube for an hour before the circuit was completed, since otherwise convection currents caused disturbance in the liquid. The electrodes were ordinarily directly connected with the terminals of the 110- or 220-volt street circuit. Owing to the high resistance of the purified colloidal solution the heating effect of the current was inappreciable.

IV. THE PHENOMENA OBSERVED IN THE MIGRATION OF COLLOIDAL GOLD.

The phenomena were found to be simplest in character when the experiments were carried out in the dark, when the electrolytes accumulating around the electrodes were washed away by a continuous current of conductivity water, and when the electrode at the top was made the cathode. In this case the colloidal gold begins at once to move away from the upper membrane with a sharp surface of demarcation between the dark red solution and the perfectly colorless liquid above. This surface moves rapidly downward at first, at a rate of about 12 cm. per hour when a potential gradient of 6 volts per centimeter is maintained. The rate of movement of the surface remains fairly constant as long as it is in the upper part of the tube, after which it continuously decreases. If the current be interrupted when the boundary has moved half way down the tube, the gold solution will be seen by its color to be more concentrated as a whole and scarcely any precipitate will be found on the lower membrane. If the migration be continued, the boundary finally reaches the lower membrane and all the gold is found as a thin layer of a red mud. When conductivity water is added to this it again passes completely in to colloidal solution. The colloid in this new solution can be again migrated down with the production of the same phenomena as before, and the mud again dissolved in water. This process can be repeated indefinitely. It is found that the conductivity of the successive colloidal solutions so obtained diminishes until it becomes not much greater than that of the water used for making up the solutions. This behavior is illustrated by the conductivity values given in Table II, which were obtained by successive migrations of dialyzed solution No. 4, dissolving the mud each time in the original volume of water having a conductivity of 1.3×10^{-6}.

TABLE II.

	$\kappa \times 10^6$.
Dialyzed solution	13.2
Solution after 1st migration	7.7
" " 2nd "	4.2
" " 3rd "	2.7
" " 4th "	2.1
" " 5th "	1.8

In these experiments running water was not used around the electrodes, but 150 cc. of conductivity water were placed at each end. The conductivity of this water increased during the fourth migration around the top electrode to 6.9 and around the bottom to 29.8, and during the fifth migration around the top to 6.5 and around the bottom to 19.9.

In the interpretation of these results it should be recalled that this decrease in conductivity can not be produced by prolonged dialysis of the solution as was shown in §I. and that, therefore, it is not due to the elimination of free electrolyte. It must, in accordance with the well-founded ideas in regard to the factors determining electrolytic conduction, be due to one or more of three other causes—to a decrease in the number of charged gold particles and of the oppositely charged free ions that may be present with them, to a decrease in the rate of migration, or to a diminished charge on each particle. The first assumption would require a coagulation or precipitation of some of the particles, and this is in contradiction with the fact that after four migrations there was no appreciable change in concentration, color, or turbidity when the solution was brought back to its original volume. That the rate of migration of the gold particles is not changed will be shown by the measurements of the rate described in §V. The conclusion seems justifiable that electric charges have been removed from the gold particles, and that they are removed in the form of ordinary ions is shown by the fact that electrolytes pass into the anode compartment in considerable quantity. The conductivity of the gold particles seems, therefore, to be due to negative ions (probably chlorine ions) associated with them, these being so firmly bound that they are not separated by dialysis, but are removed, probably at the membrane, by the electric force applied.

It was found that strong diffused daylight, falling on one side of a vertical tube in which the gold was being migrated downward, gave rise to a considerable disturbance of the boundary, causing the gold to rise rapidly on the side toward the window and to sink on the opposite side. A convection current was set up in the liquid owing to the heating effect of the sun's rays. The disturbance so produced was not appreciably lessened by surrounding the tube with a glass water-jacket. Investigated in the sun's spectrum obtained with a concave grating, it was found that the disturbance was greatest in those parts of the spectrum where the absorption of light by the solution was the strongest. Thus a red solution was disturbed only by light of wave-length less than that of the yellowish green, and the increased absorption beyond this point toward the violet end of the spectrum was marked. A violet solution was more or less sensitive to all wave-lengths, but especially to those in the yellowish green, at which point the strongest absorption also occurred.[1] Owing to the fact that the migrating surface is not always equally sensitive no quantitative results could be obtained.

This phenomena is doubtless entirely attributable to convection currents in the liquid arising from the heating effect of the light. Two facts tend to show that it is the suspended particles and not the glass that are heated. First, the effect is specific; thus it was obtained with opaque solutions like those of gold, silver, platinum and carbon, but not with transparent ones like quartz, silicic acid, gelatine, or ferric hydroxide. Second, the effect does not persist after the light is shut off, whereas, if a similar disturbance be produced by holding a lighted match a few centimeters from the tube, the effect increases several fold in the next two or three minutes after the match is removed.

Experiments on the rate of migration, conducted in the dark, show no deviation from those conducted in a room with curtains drawn; hence it is not necessary to work in complete darkness. In general, the disturbance is less the larger the bore of the tube.

Another cause of disturbance, especially marked with impure solutions, arises from the accumulation of electrolytes around the cathode, when water is not kept running past the ends of the tube. In such a case the surface of demarcation becomes very sensitive to external influences, and may break up or become indistinct.

[1] Confirmed by Ehrenhaft, Drude's *Annalen*, (4) **11**, 489 (1903).

This is especially likely to happen while the surface is in the upper third of the tube. The cause of this phenomenon becomes evident from the following consideration of the conditions that must determine the stability of the migrating surface. The rate of migration of the gold particles, as will be shown later, varies directly as the potential gradient. Now the potential gradient must evidently be constantly somewhat greater above the gold surface than immediately below it in order that the boundary may be stable, for in such a case any particles which have accidentally gotten above the surface will be carried back into it in virtue of their greater velocity. But with a constant potential difference between the ends of the tube the potential gradient in any section varies directly as the resistance of the liquid in that section, or inversely as its conductivity. We have already seen that the conductivity of a gold solution is, in part, due to the gold particles themselves and in part to free electrolytes. During the migration the concentration of the free electrolytes remains constant throughout the tube when their accumulation at the ends is prevented by running water; hence the conductivity of the liquid above the boundary is that of the free electrolytes alone, while below the boundary it is that of these electrolytes plus that of the gold particles, so the conditions of stability just stated are fulfilled. On the other hand, when the electrolytes are allowed to accumulate at the cathode they soon enter the upper portion of the migration-tube, and may increase the conductivity of the clear layer of liquid to a value above that of the gold solution below it, thus producing conditions of instability.

If, moreover, the water is not renewed around the anode, and the solution is so dilute that one can see through it, often after half an hour a darker boundary may be seen a few centimeters from the bottom moving quite rapidly up the tube. These darker surfaces do not penetrate into the clear water above the uppermost boundary, but either finally fade away in the middle of the tube or ultimately reverse the direction of their motion and reach the bottom of the tube. This phenomenon may arise from one or both of the two following causes: First, as in the case of disturbance from the cathode, the electrolytes collecting at the anode pass into the tube and decrease the resistance, and the potential gradient in its lower portion, causing the gold particles to move

more slowly than those above and hence to concentrate up to the point to which the free electrolyte has penetrated. Secondly, it may be due, in part, to the "reverse movement" frequently mentioned in the literature referred to in §II. This phenomenon requires the assumption of a change in the sign of the charge on the gold particles at the lower membrane. It will be more fully discussed below.

If, after the gold has all migrated to the lower membrane, the water around the electrodes is renewed and the current is reversed, the gold then moves steadily upward until the concentration throughout the whole tube has become nearly uniform. The surface of demarcation is faint and unstable, and if disturbed will not re-form as long as free electrolytes are uniformly distributed throughout the tube. Owing, however, to the accumulation of electrolytes around the anode at the top the surface may become stable in the upper part of the tube, its color continually growing deeper, and its rate of motion decreasing in accordance with the principles previously described (see Table XVII, page 1364).

V. THE RATE OF MIGRATION OF COLLOIDAL GOLD.

The quantitative experiments on the rate of migration were carried out in vertical tubes, arranged as described in §III. The position of the migrating boundary was read by means of a meter-stick placed beside the tube, supported in a metal base, and provided with an index finger touching the tube. It was usually possible to determine the position of the boundary to within 0.5 mm. The experiments were almost all made either in the dark or in a room with the curtains drawn. The potential difference of 110 or 220 volts, ordinarily applied from the street circuit, showed maximum variations of 10 per cent., but the variations were so irregular and of so short duration that their effect was, to a great extent, eliminated.

The experiments will be first presented which show most clearly the relation between potential gradient and rate of migration. Two tubes, each 38 cm. long, one having a diameter of 5 mm. and the other of 13 mm., fitted as usual, were filled with a dialyzed gold solution containing 680 mg. gold per liter and having a conductivity of 16×10^{-6}, and were connected in series with the

terminals of a 110-volt circuit. Hence it follows that the potential gradient in the tubes was inversely proportional to the squares of their diameters, or as $13^2 : 5^2$ or 6.76 : 1. It was found that in five and three-quarter hours the boundary moved down a distance of 14.3 cm. in the 5 mm. tube and a distance of 2.1 cm. in the 13 mm. tube, showing that the rate was 6.81 times greater in the smaller tube, in complete agreement with the relative potential gradients.

The following experiment was made with a very concentrated, dialyzed and electrically purified gold solution, containing several grams of gold per liter and having a conductivity of 8.4×10^{-6}, contained in a tube 48.5 cm. long and 2.45 cm. in diameter, with a difference of potential of 110 or 220 volts, alternately applied. In this way the rates due to the different potential gradients can be directly compared even though the rate is not constant for a constant potential difference.

TABLE III.

No.	Applied electromotive in volts.	Time intervals in minutes.	Distance intervals in centimeters.	Rate in centimeters per hour.
1	110	10	0.75	4.5
2	220	10	1.8	10.8
3	110	10	0.8	4.8
4	220	10	1.7	10.2
5	110	10	0.9	5.4
6	220	10	1.75	10.5
7	110	10	0.75	4.5
8	220	10	1.50	9.0
9	110	20	1.10	3.3
10	220	16	3.50	8.1
11	110	9	0.50	3.3
12	220	10	1.15	6.9
13	110	10	0.40	2.4

The accuracy with which the surface could be read is indicated by the number of decimals used in expressing the distances. A comparison of these results with those obtained in a similar experiment with a constant potential difference (see Table IV) shows that for the accuracy obtained the rate varies directly as the potential gradient for the first eight readings. The sudden drop noted at reading No. 9 is attributable to the reverse effect, discussed

farther on. It is noteworthy that beyond this point the relative rate of migration is distinctly less for the smaller potential.

The next experiments show the rate of migration during the process of purification of gold solutions by the successive downward migrations and re-solutions described in §IV. The three following experiments were made with dialyzed solution No. 4 in a tube 36.5 cm. long and 2.75 cm. in diameter. A potential difference of 220 volts was applied. Conductivity water was kept slowly flowing by both ends of the tube. The room was darkened by drawing the curtains. The gold was migrated down three times in succession and twice redissolved in conductivity water. The conductivity of the gold solution (κ_s) and that (κ_w) of the water in the tube after gold had migrated out of it was each time determined.

The first column gives the number of the reading, the second the total time in hours, the third the distance from the upper membrane to the boundary, and the fourth the rate in centimeters per hour between the successive readings.

TABLE IV.

Solution No. 4. First migration down. $\kappa_s = 12.7 \times 10^{-6}$; $\kappa_w = 3.7 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.167	2.00	12.00
2	0.33	4.10	12.60
3	0.50	5.80	10.20
4	0.67	8.00	13.20
5	0.83	10.30	13.80
6	1.00	12.35	12.30
7	1.17	13.60	7.50
8	1.42	15.50	7.60
9	1.58	16.35	5.10
10	1.75	17.20	5.10
11	2.00	18.25	4.20
12	2.25	19.05	3.20
13	2.67	20.45	3.36
14	3.25	22.15	2.91
15	4.25	24.25	2.10
16	4.83	25.30	1.80
17	5.83	26.20	0.90
18	6.17	26.40	0.60

TABLE V.

Solution No. 4. Second migration down. $\kappa_s = 7.8 \times 10^{-6}$; $\kappa_w = 3.9 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.267	2.70	10.13
2	0.43	4.25	9.30
3	0.60	5.65	8.40
4	0.77	7.00	8.10
5	0.93	8.10	6.60
6	1.13	9.20	5.50
7	1.33	10.25	5.25
8	1.58	11.55	4.80
9	1.92	12.85	4.35
10	Surface suddenly broken up at $t = 2.4$, distance = 15.		
11	5.08	17.85	2.50
12	5.58	19.20	2.70
13	6.08	21.40	4.40
14	6.75	23.60	3.30
15	7.25	25.10	3.00
16	7.75	26.05	1.90

TABLE VI.

Solution No. 4. Third migration down. $\kappa_s = 5.1 \times 10^{-6}$; $\kappa_w = 2.1 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.167	1.90	11.40
2	0.35	3.90	10.90
3	0.52	5.60	10.20
4	0.68	7.10	9.00
5	0.85	8.70	9.60
6	1.27	12.10	8.16
7	1.52	13.50	5.60
8	1.78	15.15	6.19
9	2.04	16.50	5.40
10	2.28	17.65	4.60
11	2.53	18.80	4.60
12	2.95	20.60	4.32
13	3.38	22.30	3.92
14	3.88	24.15	3.70
15	4.60	26.20	2.86
16	5.93	28.90	2.03

The following series of experiments were made like the preceding ones, except that they were carried out in complete darkness and that the water was not flowing around the ends of the tube. The migration was, moreover, repeated five times. The tube used was 48.5 cm. in length and 2.45 cm. in diameter. Another portion of the same gold solution was used for these experiments.

TABLE VII.

Solution No. 4. First migration down. $\kappa_s = 13.2 \times 10^{-6}$; $\kappa_w = 4.0 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.55	3.5	6.4
2	0.97	6.4	6.8
3	1.47	10.3	7.8
4	1.80	13.2	8.7
5	2.13	16.6	10.2
6	2.38	18.5	7.6
7	2.63	20.0	6.0
8	3.05	21.7	4.8
9	3.55	23.3	3.2
10	4.05	24.6	2.6
11	4.38	25.3	2.1[1]
12	32.38	41.8	1.03

[1] Change water at ends.

TABLE VIII.

Solution No. 4. Second migration down. $\kappa_s = 7.6 \times 10^{-6}$; $\kappa_w = 2.8 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.67	4.6	6.90
2	1.00	6.7	6.30
3	1.67	10.6	5.85
4	2.38	14.1	4.90
5	2.72	15.7	4.80
6	3.22	18.0	4.60
7	3.72	19.9	3.80
8	4.22	21.7	3.60
9	4.72	23.4	3.00
10	7.13	30.8	3.06

TABLE IX.

Solution No. 4. Third migration down. $\kappa_s = 4.2 \times 10^{-6}$; $\kappa_w = 2.5 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.317	3.00	9.46
2	0.52	4.80	9.00
3	0.85	7.70	8.70
4	1.78	14.80	7.61
5	2.02	16.40	6.86
6	2.72	20.45	6.43
7	3.22	22.90	4.90
8	5.13	30.10	3.76
9	5.72	32.15	3.51
10	7.92	39.00	3.11

TABLE X.

Solution No. 4. Fourth migration down. $\kappa_s = 2.7 \times 10^{-6}$; $\kappa_w = 2.4 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	2.05	8.20
2	0.50	4.00	7.80
3	0.75	6.05	8.20
4	1.58	13.00	8.34
5	2.08	17.25	8.50
6	2.58	21.15	7.80
7	3.08	24.00	5.70
8	4.52	29.60	3.91
9	5.72	33.05	2.87
10	8.15	38.15	2.51
11	10.62	43.60	1.80

Final κ aq. top (150 cm^3.) $= 6.9 \times 10^{-6}$.
Final κ aq. bottom (150 cm^3.) $= 29.8 \times 10^{-6}$.

TABLE XI.

Solution No. 4. Fifth migration down. $\kappa_s = 2.1 \times 10^{-6}$; $\kappa_w = 2.1 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimers per hour.
1	0.25	2.30	9.2
2	0.50	4.20	7.6
3	0.75	6.25	8.2
4	1.00	8.25	8.0
5	1.25	10.30	8.2
6	1.50	12.35	8.2
7	1.72	14.15	8.3
8	1.97	16.30	8.6
9	2.22	18.50	8.8
10	2.47	20.50	8.0
11	2.72	22.65	8.6
12	2.97	24.60	7.8
13	3.85	31.20	7.5
14	4.10	32.70	6.0
15	5.27	39.50	5.8
16	6.19	44.50	5.5
17	6.69	46.30	3.6

Final κ aq. top (150 cm^3.) $= 6.5 \times 10^{-6}$.
Final κ aq. bottom (150 cm^3.) $= 19.9 \times 10^{-6}$.

Attention may first be directed to the comparative rates of migration at the beginning of the experiments when the potential gradient throughout the solution is uniform and is readily calculated from the applied electromotive force and the length of the tube. It will be seen that even in the early stages the rates in most cases decrease. To determine the true initial rate we have

extrapolated for time zero from the first few rates under the assumption that the change in rate is a linear function of the time. The values so obtained from the results of the three experiments of the first series are 12.0, 11.0 and 11.8 cm. per hour respectively, and the potential gradient in these cases was 6.03 volts per centimeter. The average of these values corresponds to 1.92 cm. per hour for a potential gradient of 1 volt per centimeter. The initial rates for the last four experiments of the second series, similarly extrapolated, are 8.0, 9.8, 8.2 and 8.3 cm. per hour, with a potential gradient of 4.54 volts per centimeter. The average of these values corresponds to 1.89 cm. per hour for unit potential gradient, in approximate accordance with the result of the first series. The agreement of the rates in the separate experiments of either series shows that the rate of migration is independent of the conductivity of the gold solution and of the extent to which it has been freed from electrolytes. Since on each migration only an insignificant quantity of gold is precipitated in an insoluble form on the lower membrane and, therefore, the solution always contains the same quantity of gold and since there is no free electrolyte in the dialyzed solution used at the start in excess of that present in the water outside the dialyzer, and since at any rate the free electrolytes must have been almost wholly removed after the first migration when the few cubic centimeters of soluble mud were dissolved in conductivity water, this decrease in conductivity of the gold solution must be due to a decrease in the total charge on the particles, arising from the separation of the ions of hydrochloric acid associated with them, indicating either a partial coagulation of the gold insufficient to increase the turbidity of the solution, or that more than one ion was originally associated with each particle. Since the particles are negatively charged, chlorine ions are probably directly attached to them, while hydrogen ions remain in the neighborhood to maintain the electrical neutrality of the solution.

Except in the first experiment of each series the rates of migration show a steady decrease, usually, however, showing a rather sudden decrease at a point from one-third to one-half the distance down the tube. The gradual decrease in the rates is due to the fact that the total resistance of the continually lengthening layer of clear water above the boundary continually increases, whereas the specific resistance of the gold solution continually decreases,

owing to the fact, already noted, that the concentration of the gold solution continually increases during the migration. Hence the potential gradient in the gold solution continually decreases, and, consequently, the rate of migration. This increase in the conductivity of the migrating solution may be determined approximately by pipetting it out after the boundary has moved part way down the tube. Thus in one experiment the specific conductivity of the gold solution, concentrated by the migration, was found to have increased 26 per cent. after its average concentration had increased 37 per cent. It has been found, in fact, that a formula based on the assumption that the gold below the boundary remains uniformly distributed throughout the experiment and that its specific conductivity varies directly as its concentration, while the specific conductivity of the water above the boundary remains constant throughout the experiment at the value actually determined by pipetting it out at the end of the experiment, enables one to predict to within a few millimeters the total distance the boundary will have moved during any interval of time. It will be shown, however, that the concentration of the gold solution does not remain uniform and that other factors materially influence the rate when the potential gradient is small. Hence the formula just mentioned can be only an approximation, which we allude to, however, in support of the ideas regarding the conditions determining the stability of the boundary enunciated in §IV.

The irregularity in the beginning, rates of the first experiment of the second series (Table VI), is attributable to the accumulation of electrolytes around the cathode in accordance with principles already discussed (page 1348).

The magnitude of the sudden drop in the rate between successive readings, as well as the percentage of the distance from the top of the tube at which it occurs in the foregoing experiments, is shown in Table XII.

An inspection of the following tables containing the rates will show that no other changes in the rate for smilar intervals of time are nearly so great as those here set opposite the percentage distances from the top, as is also shown in the foregoing table for the readings adjacent on either side to the reading at which the reverse effect occurs. It is plain that the method of making the readings precluded the possibility of detecting the maximum rate of de-

TABLE XII.

Series 1.

Table No.	Reading No.	Percentage change of rate per minute.	Percentage distance from top of tube.	Conductivity of gold solution × 10^6.
	5–6	—1.1		
IV	6–7	—3.9	34	12.7
	7–8	+0.1		
V	10–11	Surface broken up	(39)	7.8
	5–6	—0.6		
VI	6–7	—2.1	33	5.1
	7–8	+0.5		

Series 2.

	4–5	+0.8		
VII	5–6	—1.7	34	13.2
	6–7	—1.4		
	5–6	—0.1		
VIII	6–7	—0.6	37	7.6
	7–8	—0.1		
	5–6	—0.1		
IX	6–7	—0.8	42	4.2
	7–8	—0.2		
	5–6	—0.3		
X	6–7	—0.9	44	2.7
	7–8	—0.3		
	12–13	—0.1		
XI	13–14	—1.3	64	2.1
	14–15	—0.1		

crease, such as more frequent readings would have disclosed. The position at which this sudden decrease occurs is usually about one-third the distance down the tube, but it is still farther down in extremely pure solutions. This sudden decrease in the rate may be due to one or both of the two following causes: (1) To a sudden decrease in the potential gradient at the boundary, due to the arrival of a denser layer of hydrogen ions from the anode; (2) to a decrease in the resultant negative charge on the gold in the boundary, considered as a whole, due to the arrival of positively charged gold particles originating at the anode membrane. It was found by actual measurement of the con-

ductivity of the electrically concentrated gold solution after a migration part way down the tube that the conductivity of the gold solution had greatly increased. From a consideration of the observed rates of migration in the different sections of the tube, and from a consideration of the relative values of κ_s and κ_w, already defined, as well as from the approximate agreement of the rates of migration with those calculated from the formula mentioned on page 1356, it may easily be seen that the average potential gradient in the electrically concentrated gold solution up to the time the reverse effect occurs might well be only one-half or one-third the average potential gradient at the boundary up to that time. It will be shown that the rate of migration of the boundary is approximately that of the univalent ions of neutral inorganic salts. Hence the observed sudden retardation in the rate of migration, if due to any influence originating at the anode, must be due to the arrival of hydrogen ions. This will appear more fully farther on.

It will now be shown that any increase in the conductivity at the boundary produced by the arrival of hydrogen ions from the anode, with consequent decrease in the potential gradient at that point, is insufficient to account for the observed phenomena. In diute solutions the motion of the boundary is either entirely arrested at a point about one-fourth the way down the tube, or its direction of motion reversed. In cases where the boundary thus becomes stationary the gold is slowly carried to the lower membrane in insensible portions, the color below the boundary gradually fading away in the next few hours.[1] This effect could be due only to a complete neutralization of the particles forming the boundary. The actual simultaneous migration of gold up the tube as a dense layer, starting at the bottom, has already been alluded to (page 1348) and considered more fully in §XIII. This behavior can be explained only on the assumption that the hydrogen ions carry the gold along with them to some extent. It is plain that in so far as positively charged particles thus brought to the boundary tend to neutralize its charge, taken as a whole, the rate of migration would not be dependent solely on the potential gradient.

It was found in experiments similarly conducted that the initial rate is independent of the concentration of the gold solution for

[1] See Blake: *Am. J. Sci.*, **16**, 434.

variations of a hundredfold. So, also, gold solution No. 3, after treatment with hydrogen under a pressure of two feet of water for times varying from two hours to two months, gave the same initial rate of migration from the cathode as before such treatment, and the same as gold solution No. 4. The same initial rate in the same direction was obtained when an excess of ammonia was added to the solution, with or without the hydrogen. The red gold solution formed by treating coagulated blue gold with ammonia (see page 1341) also migrated from the cathode with nearly the same initial rate.

It was found that gold solution No. 2, which was originally somewhat turbid, migrated as usual for the first ten days. Thereafter part of the gold was coagulated and rendered insoluble by each successive migration, the gold thus thrown out forming a red precipitate with network structure on the lower membrane. This red precipitate turned blue on drying, as does the soluble red mud, and as does pure red silver.[1] The following tables of rates, obtained with solutions No. 2, during the second and third migrations, may be given to illustrate this behavior, more especially as it is also the behavior of most colloidal solutions. The tube was 33.1 cm. long and 2.75 cm. in diameter. The water at the ends, though not running, was kept below 10×10^{-6}. The potential difference was 110 volts. Strong light was excluded from the room.

Practically none of the gold was precipitated during the first migration, which gave decreasing rates after the first increase which occurs in impure solutions (see Table VI). A considerable part of the gold was precipitated in each of the subsequent experiments, one-sixth having been rendered insoluble in all three migrations. It is evident that this precipitation of the gold would render its concentration in the lower part of the tube less than it would otherwise have been, thus lowering the conductivity and increasing the potential in this part of the tube, and lessening the retardation of the boundary by positively charged particles originating at the anode membrane. As a matter of fact, no increase in the depth of color of the solution during the migration can be seen with gold solutions showing such constant rates nor with most of the other colloidal solutions tested. It is doubtless for

[1] **Blake**: *Am. J. Sci.*, **16**, 282 (1903).

TABLE XIII.

Solution No. 2. Second migration down. $\kappa_s = 7.3 \times 10^{-6}$; $\kappa_w = 2.7 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.	$\frac{\text{Distance}}{\text{Time}}$.
1	0.38	2.05	5.35	5.35
2	0.55	3.00	5.70	5.45
3	0.72	4.05	6.30	5.62
4	0.88	5.07	6.12	5.76
5	0.98	5.71	6.40	5.83
6	1.20	7.00	5.95	5.83
7	1.37	8.00	6.00	5.84
8	1.57	9.30	6.50	5.92
9	1.73	10.40	6.60	6.01
10	1.90	11.45	6.30	6.03
11	2.07	12.61	6.96	6.09
12	2.28	14.05	6.65	6.17
13	2.48	15.65	8.00	6.31
14	2.68	17.15	7.50	6.40
15	2.85	18.90	10.50	6.63
16	3.02	20.00	6.60	6.62
17	3.18	20.60	3.60	6.48
18	3.35	21.15	3.30	6.31
19	3.52	21.61	2.76	6.14
20	3.68	22.11	3.00	6.01
21	4.13	23.25	2.53	5.63
22	4.38	23.85	2.40	5.45
23	4.63	24.20	1.40	5.23
24	5.13	25.02	1.64	4.88
25	5.67	25.90	1.65	4.57
26	7.75	28.10	1.06	3.63

TABLE XIV.

Solution No. 2. Third migration down. $\kappa_s = 3.8 \times 10^{-6}$; $\kappa_w = 2.2 \times 10^{-6}$.

No.	t. Time in hours.	s. Distance in centimeters.	Rate in centimeters per hour.	$\frac{\text{Distance}}{\text{Time}}$.
1	0.33	1.83	5.32	5.32
2	0.50	2.78	5.70	5.56
3	0.67	3.78	6.00	5.64
4	0.83	4.80	6.14	5.78
5	1.00	5.73	5.58	5.73
6	1.22	7.03	6.00	5.76
7	1.38	8.10	6.42	5.87
8	1.58	9.37	6.35	5.93
9	1.75	10.33	5.76	5.90
10	2.00	12.13	7.20	6.07
11	2.17	13.15	6.12	6.07
12	2.33	14.13	5.88	6.06
13	2.58	15.83	6.80	6.14
14	3.42	19.73	4.68	5.77
15	3.92	21.03	2.60	5.37
16	4.28	22.13	3.00	5.17
17	4.78	23.18	2.10	4.85
18	5.50	25.33	2.63	4.52
19	7.43	28.03	1.47	3.77

these reasons that the rate is so nearly constant. The initial values correspond to a rate of 1.60 cm. per hour for unit potential gradient.

In experiments made a few days later than the foregoing the first migration gave nearly constant rates and an insoluble red precipitate formed on the lower membrane, showing that the solution itself was unstable, a property indicated by its original turbidity.

VI. DIFFUSION OF COLLOIDAL GOLD.

The gold from a portion of solution No. 4 was migrated clear to the bottom of the tube, which was 33.1 cm. long and 2.75 cm. in diameter. The potential difference of 220 volts was left on twelve hours longer and then the circuit was broken. The gold began to diffuse quite rapidly up the tube, the boundary becoming faint and indistinct. After a few hours the concentration of the gold in the boundary increased until no irregularities in the density of the gold solution could be detected. Thereafter the surface remained sharp and perpendicular to the axis of the tube for weeks. After the first week a faint pink tint could be detected in the water above the gold. The experiment was carried out in a room with drawn curtains. The ends of the tube were left in contact with water, as in the migration, fresh water having been added shortly before the circuit was broken. The rates of diffusion are given in the following tables:

TABLE XV.

Time in hours.	Distance from bottom of tube in centimeters.	Rate in centimeters per hour.	k.	Variations of k for 1 millimeter of distance.	
4.5	0.60	0.13	0.040	Day (surface indistinct)	
21.5	1.20	0.03	0.034	Night	0.039
31.5	1.55	0.03	0.038	Day	
46.5	2.20	0.04	0.052	Night	
55.5	2.40	0.02	0.052	Day	
70.5	2.65	0.02	0.050	Night	
78.5	2.90	0.03	0.054	Day	0.050
95.5	3.20	0.02	0.052	Night	
119.0	3.40	0.01	0.049	Day and night	
126.0	3.60	0.03	0.051	Day	
142.0	3.80	0.01	0.051	Night	
151.0	3.90	0.01	0.050	Day	
165.5	4.00	0.01	0.048	Night	
174.5	4.10	0.01	0.048	Day	
190.5	4.20	0.01	0.049	Night	
199.5	4.30	0.01	0.046	Day	
214.0	4.30	0.00	0.043	Night	
237.5	4.50	0.01	0.043	Day and night	0.045

The following experiment was similarly conducted with the gold migrated downward from a portion of solution No.3 in a tube 36.5 cm. long and 2.45 cm. in diameter. The experiment was carried out in the dark.

TABLE XVI.

Time in hours.	Distance from bottom of tube in centimeters.	Rate in centimeters per hour.	k.	Variation of k for 1 mm. of distance.	Temperature water at bottom.
				Surface	
5.0	1.20	0.240	0.144	indistinct	21.0
9.5	1.45	0.033	0.105	0.096	20.5
24.5	2.05	0.040	0.086		22.0
33.0	2.30	0.029	0.080		22.8
49.0	2.80	0.031	0.080		20.8
59.5	3.15	0.034	0.083	0.079	20.5
74.0	3.45	0.021	0.080		20.0
81.5	3.60	0.020	0.079		20.5
96.0	3.90	0.021	0.079		20.6
106.0	4.05	0.015	0.077		20.7
119.0	4.35	0.023	0.080		21.0
128.0	4.45	0.011	0.078		18.0
145.0	4.75	0.018	0.078		19.4
155.0	4.85	0.010	0.076		19.4
169.0	5.05	0.014	0.075		18.7
178.0	5.20	0.017	0.076		18.8
192.0	5.40	0.014	0.076		18.0
200.0	5.45	0.006	0.074		19.5
215.0	5.60	0.010	0.073		19.0
224.0	5.70	0.011	0.073		18.2
239.0	5.80	0.007	0.070	0.073	18.0

If this is a true diffusion of the gold, the rate should vary as its concentration in solution. Under the given conditions the concentration of the gold solution would vary as $1/s$, where s is the distance of the moving boundary from the lower membrane.

Hence putting

$$\frac{ds}{dt} = \frac{k}{s}, \qquad (1)$$

when k is a constant, we have

$$k = \frac{s^2}{2t},$$

if $s = 0$ when $t = 0$. The values of k thus calculated are included in the tables and are constant within 2 or 3 mm., although

the value of k tends to decrease. The beginning values are rendered uncertain by reason of the slight disturbance in the surface produced by the rapid diffusion at first as well as by the fact that the lower membrane is slightly convex downward, owing to the weight of the liquid. The bulk of the "solid" red gold at the start introduces errors which may be neglected until great accuracy is desired. The relative values of the constant in the two experiments ($80/50 = 1.6:1$) is in approximate agreement with the amounts of gold deposited on the lower membranes from the two solutions, which were in the ratio of 2.4:1. This constant represents the rate of diffusion for the concentration existing in the gold solution, if uniform, when the boundary is 1 cm. from the bottom, as may readily be seen by putting $s = 1$ in formula (I). The rates for this concentration, equal to 4.82 and 11.68 grams of gold per liter, respectively, are of the same order of magnitude as those obtained with electrolytes in concentrated solution diffusing into pure water. It was found that with ordinary precautions these solutions, even though containing several grams of gold to the liter, gave no measurable lowering of the freezing-point of water and no measurable osmotic pressure.

It is plain that this diffusion of the gold would lessen the rate of migration downward under the conditions of the foregoing experiments, and that the percentage retardation due to this cause would increase as the potential gradient falls. This is indicated in the last few readings of Table III, as already pointed out, the concentration of the gold in that experiment having been very great.

VII. THE EFFECT OF GRAVITY ON THE RATE OF MIGRATION.

The phenomena occurring in the upward migration of colloidal gold under the given conditions are described in § IV. The following downward and upward migrations were made with solution No. 2 contained in a tube 33.1 cm. long and 2.75 cm. in diameter, with a potential difference of 110 volts. After the first migration down, the water at the ends was changed and the current reversed, giving the first migration up. The water at the ends was again changed and the gold migrated down again. Then the water at the ends was changed again, giving the second migration up. The amount of electrolyte eliminated at the ends continually diminished. Strong light was excluded from the room.

TABLE XVII.

Solution No. 2.

First migration up.

No.	Distance from bottom in centimeters.	Rate in centimeters per hour.
..	4.10	....
1	7.50	2.46
2	8.68	2.95
3	9.60	2.76
4	10.55	2.85
5	Surface broken up.	
6	21.45	3.72
7	22.20	4.50
8	22.80	3.00
9	23.57	3.85
10	24.60	3.43
11	28.70	2.90
12	29.60	2.70
13	30.70	2.64

TABLE XVIII.

Second migration up.

No.	Time in hours.	Distance from bottom in centimeters.	Rate in centimeters per hour.
..	....	4.55	....
1	0.25	5.10	2.20
2	2.07	10.90	3.20
3	2.32	11.90	4.00
4	2.57	12.95	4.20
5	2.82	13.90	3.80
6	3.07	14.90	4.00[1]
7	3.32	15.85	3.80
8	3.57	16.60	3.00
9	3.82	17.60	4.00
10	4.07	Unreadable.	....

[1] Surface disturbed.

The following experiment was similarly conducted with solution No. 4 after the first migration down. The tube was 36.5 cm. long and 2.75 cm. in diameter, the potential difference 220 volts. The experiment was carried out in the dark.

TABLE XIX.

Solution No. 4. First migration up.

No.	Time in hours.	Distance from bottom in centimeters.	Rate in centimeters per hour.
1	0.25	1.9	7.6
2	0.67	4.8	6.8
3	0.92	6.8	8.0
4	1.17	8.5	6.8
5	1.47	10.5	6.7
6	1.92	14.1	8.0
7	2.25	Surface broken up.	

The average rate of migration upward, derived from the nearly constant rates of Table XVIII, is 3.42 cm. per hour for a potential gradient of 3.32 volts per centimeter, if uniform, corresponding to a rate of 1.03 cm. per hour for unit potential gradient. The nearly constant rates given in Table XIX give an average of 7.34 cm. per hour for a potential gradient of 6.03 volts per centimeter, or 1.22 cm. per hour for unit potential gradient. The rates of migration downward for the same potential gradients were 1.60 cm. and 1.90 cm. per hour, respectively. There seems, there-

fore, to be a gravity effect on the rate of migration which increases with the potential gradient. We have seen that with zero potential gradient the surface slowly moves up the tube owing to diffusion. With small potential gradients amounting to a few tenths of a volt per centimeter the difference in the rate down and up is scarcely distinguishable. The results are not sufficiently extended, however, to permit one to draw any certain conclusion beyond this, that the gravity effect is not larger than half the difference between the rates up and down, or 0.34 cm. per hour for a potential gradient of 6.03 volts per centimeter. Subtracting this from 1.90 cm. per hour we obtain 1.56 cm. per hour, or 0.00043 cm. per second, the velocity of the sodium ion. The results are not sufficiently accurate to enable one to say that the rate of migration of colloidal gold differs from that of any of the ions of neutral inorganic salts of univalent elements.

The constancy of the rate in the upward migrations is conditioned by the fact that the potential gradient in the pure water above the gold is nearly uniform and that the most advanced gold particles practically move under that potential gradient.

It was found that a solution of red gold containing 0.68 gram per liter falls into pure water at the rate of 1.3 cm. per minute. The phenomenon could not be distinguished from a similar experiment made with a solution of potassium permanganate containing the same amount of dissolved substance per liter. Since this rate is so much greater than the rate of migration with the potentials usually applied, it is evident why the current cannot raise the gold from the lower membrane when the cathode is at the bottom.[1]

VIII. COLLOIDAL PRUSSIAN BLUE.

It was of considerable interest to apply the foregoing method of investigation to other colloids in order to test the generality of its applicability and, if possible, to discover new relations between the properties of these substances. Accordingly, the following experiments were made with colloidal Prussian blue, formed by the action of ferric chloride on an excess of potassium ferrocyanide in solution. The resulting precipitate was purified to some extent by three or four filtrations with a porous cell. A little of the blue material went into the cell, but most of it remained outside. One gram of this material, air-dried, was dis-

[1] *Cf.* p. 1341.

solved in a liter of ordinary distilled water ($\kappa_w = 15 \times 10^{-6}$), the conductivity of the resulting solution being 187.8×10^{-6}. The tube used in these experiments was 33.1 cm. in length and 2.75 cm. in diameter. The voltage between the terminals was 220, with the cathode at the top. Fifty cc. of water were placed at each end of the tube. Strong light was excluded from the room.

TABLE XX.

Prussian blue solution. First migration down.

$\kappa_s = 187.8 \times 10^{-6}$; $\kappa_w = 11.0 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.167	2.0	12.0
2	0.33	4.0	12.0
3	0.50	5.9	11.4
4	0.67	7.7	10.8
5	0.83	9.3	9.6
6	1.00	10.7	8.4
7	1.25	12.8	6.8
8	1.50	13.7	5.2
9	2.25	16.3	3.1
10	2.58	17.1	2.4
11	3.08	17.9	1.6
12	3.83	19.2	1.7
13	4.17	19.5	0.90
14	4.83	20.2	1.05
15	5.67	21.0	0.96
16	6.33	21.7	1.05
17	8.50	23.5	0.81
18	11.00	24.8	0.52
19	22.00	28.5	0.16

TABLE XXI.

Prussian blue solution. Second migration down.

$\kappa_s = 56.5 \times 10^{-6}$; $\kappa_w = 4.0 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.28	3.3	11.8
2	0.50	4.3	4.6
3	0.83	5.4	3.3
4	1.83	8.0	2.6
5	2.17	8.9	2.7
6	2.67	9.9	2.0
7	4.25	12.7	2.0
8	5.25	14.3	1.6
9	6.75	16.2	1.3
10	7.75	17.3	1.1
11	24.42	30.5	0.46

TABLE XXII.

Prussian blue solution. Third migration down.

$\kappa_s = 16.4 \times 10^{-6}$; $\kappa_w = 2.6 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.183	2 3	12.5
2	0.33	3.4	7.3
3	0.53	4.7	6.6
4	0.70	5.6	5.4
5	1.17	7.7	4.5
6	1.50	8.9	3.6
7	1.83	10.1	3.6
8	2.42	11.9	3.09
9	3.08	13.5	2.40
10	4.00	15.3	1.96
11	4.75	16.6	1.73
12	5.75	18.3	1.70
13	6.83	20.2	1.75
14	8.08	22.1	1.52

TABLE XXIII.

Prussian blue solution. Fourth migration down.

$\kappa_s = 6.7 \times 10^{-6}$; $\kappa_w = 3.4 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.15	2.1	14.0
2	0.25	3.2	11.0
3	0.35	4.3	11.0
4	0.50	5.5	8.0
5	0.75	7.6	8.4
6	1.00	9.5	7.6
7	1.83	14.4	5.9
8	2.33	16.7	4.6
9	3.00	19.2	3.75
10	3 67	21.3	3.45
11	4.33	23.2	2.85
12	5.08	25.0	2.16
13	6.67	28.1	1.96

These results confirm the indications obtained with gold both as to the general march of the experiments and the magnitude and direction of the rate of migration. The initial values in the four experiments give an average rate of 1.88 cm. per hour for unit potential gradient, whereas that obtained for gold was 1.90 cm. per hour for substantially the same potential gradient. The reverse effect is especially pronounced, more particularly as it

occurs so near the beginning of the experiment. This is best seen in the last migration, since the solution was at first so impure that the heating effect of the current and other disturbing influences due to electrolytes might not be negligible. In the last experiment the reverse effect (reading No. 3) occurred after 0.35 hour at a point 4.3 cm. down the tube, whereas the hydrogen ions, under the given potential gradient, 6.65 volts per centimeter, if uniform, would have moved up to this point in exactly the same time. The potential gradient in the Prussian blue solution would have changed but little in that time.

Hence it seems certain that the sudden decrease in the rate of migration attributed to the reverse effect, both of colloidal gold and of colloidal Prussian blue, is due to the arrival of hydrogen ions liberated at the anode, whether with or without associated colloidal particles.

IX. COLLOIDAL PLATINUM.

Platinum electrodes were sparked for about twenty minutes under water having a conductivity of 1.1×10^{-6}. The resulting solution had a conductivity of 2.9×10^{-6}. This solution was placed in a tube 33.1 cm. long and 2.75 cm. in diameter, and joined to the 220-volt circuit with the cathode at the top. After the platinum had been migrated clear to the bottom of the tube the water at the ends of the tube was changed and the platinum migrated up. The experiments were carried out in the dark.

TABLE XXIV.

Platinum solution, fresh.

First migration down. $\kappa_s = 2.9$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	2.2	8.8
2	0.50	4.5	9.2
3	1.00	9.2	9.4
4	1.50	14.1	10.2
5	2.00	18.5	8.4
6	2.35	20.9	6.9
7	3.93	28.0	4.9

TABLE XXV.

First migration up.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.88	5.2	5.9
2	1.13	6.8	6.4
3	1.52	8.6	4.7
4	1.95	10.9	5.3
5	2.85	15.3	4.9[1]
6	3.33	17.1	4.3[1]
7	3.83	20.6	7.0[1]
8	4.33 Surface broken up		

[1] Surface irregular.

The following experiments were similarly conducted with part of the same solution two days later, after the particles visible under the microscope had largely settled out and the conductivity had increased to 4.6×10^{-6}.

TABLE XXVI.

Platinum solution, two days old.

First migration down. $\kappa_s = 4.6 \times 10^{-}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	2.7	10.8
2	0.50	5.1	9.6
3	0.75	8.2	12.4
4	1.00	10.8	10.4
5	1.80	18.8	10.0
6	2.10	20.2	4.7
7	2.35	21.1	3.6
8	2.63	22.1	3.4
9	2.85	22.8	3.2

TABLE XXVII.

First migration up.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	1.7	6.8
2	0.50	3.6	7.6
3	0.75	5.1	6.0
4	1.00	6.4	5.2
5	1.27	7.7	4.9
6	1.50	9.0	5.6
7	1.75	10.1	4.4[1]
8	2.00	Unreadable	..

[1] Surface irregular.

The rates obtained in both experiments are a little less than those obtained for gold, both in the migration down and in the migration up, being respectively 1.5 cm. and 0.95 cm. per hour for unit potential gradient, whereas the corresponding rates for gold for substantially the same potential gradient were 1.90 and 1.22 cm. per hour. The difference in the initial rates in the two experiments is so great, however, that little significance can be attached to the variation pointed out. The gravity effect is about the same, being 0.28 cm. per hour for a potential gradient of 6.65 volts per centimeter. The reverse effect is marked in the experiment recorded in Table XXVI.

X. QUARTZ SUSPENSIONS.

Rock quartz was pulverized in an agate mortar and suspended in conductivity water. It was found that most of the powder settled out over night, forming one or more sharp surfaces of demarcation, but leaving a uniform turbidity behind. Particles showing the Brownian movement were readily visible under the microscope in all these surfaces. The effect is especially beautiful in reflected sunlight, and is visible between crossed nicols. On adding a little barium chloride solution the Brownian movement was instantly stopped and the quartz precipitated, although no aggregates seemed to form. In the following migration experi-

ments, two suspensions of powdered quartz were used, each of which had stood over night. The supernatant liquid, containing one surface of demarcation (which settled at the rate of 0.3 cm. per hour), as well as the uniform turbidity, was decanted and migrated down in a tube 33.1 cm. long and 2.75 cm. in diameter. The difference of potential was 220 volts, with the cathode at the top. The experiments were conducted in ordinary daylight.

TABLE XXVIII.

Quartz suspension No. 1. First migration down. $\kappa_s = 5.6 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.30	2.5	8.3
2	0.45	3.9	9.3
3	0.62	5.9	12.0
4	0.78	7.9	12.0
5	0.92	9.8	14.25
6	1.20	11.9	7.4
7	2.20	16.1	4.2
8	2.50	17.0	3.0
9	2.83	17.6	1.8
10	3.47	18 6	1.8
11	4.28	19.8	1.5
12	4.70	20.4	1.03
13	4.95	20.7	1.2
14	5.95	22.1	1.4
15	7.17	24.0	1.6
16	7.67	24.6	1.2

TABLE XXIX.

Quartz supension No. 2.

First migration down. $\kappa_s = 3.8 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.28	2.5	8.8
2	0.42	3.8	9.7
3	0.62	5.7	9.5
4	0.92	8.5	8.0
5	1.12	10.6	10.5
6	1.37	13.8	12.8
7	1.70	17.7	11.7
8	1.92	20.4	12.5
9	2.08	22.3	11.4
10	2.25	23.8	9.0
11	2.43	25.1	7.1

TABLE XXX.

First migration up.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.12	0.8	6.9
2	0.23	1.6	6.0
3	0.35	2.4	6.0
4	0.50	3.3	6.0
5	0.70	4.3	5.0[1]
6	1.00	5.7	4.7[1]
7	1.52	8.4	5.2[1]
8	2.33	13.1	5.8
9	2.70	15.7	7.1
10	2.83	16.8	8.2
11	3.33	20.0	6.4

[1] Surface irregular.

TABLE XXXI.

Quartz suspension No. 2.

Second migration down.

$\kappa_S = 1.9 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	2.5	10.0
2	0.40	3.7	8.0
3	0.57	5.3	9.6
4	0.87	8.0	9.0
5	1.00	9.3	9.7
6	1.25	12.0	10.8
7	1.45	14.1	10.5
8	2.25	20.5	8.0
9	2.65	23.1	6.5
10	3.00	25.3	6.3
11	3.67	28.8	5.25

TABLE XXXII.

Second migration up.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	1.23	6.7	5.5
2	1.90	10.9	6.3
3	2.48	14.0	5.3
4	2.93	15.5	3.3
5	3.37	18.0	5.8
6	4.03	20.7	4.05
7	4.53	Surface irregular.	

The results obtained with quartz are practically identical with those obtained with platinum, both down and up, even including the reverse effect (Table XXVIII, reading No. 5). In all the other experiments with quartz the formation of a precipitate on the lower membrane could readily be observed from the start, although the effect of settling would be inappreciable in the given time. It is probable that the unstable particles present in the quartz and platinum hydrosols were without effect on the rate of migration, since the migrating surface, both down and up, would be composed of the stablest particles.

The decrease in the rate going up, which usually occurs after the first few readings, is probably due to the effect of the hydrogen ions coming down the tube, thus lessening the potential gradient by their presence.

The results obtained with platinum and quartz seem quite remarkable. We have here, especially with quartz, the migration of particles whose diameter is approximately 1 μ with a velocity almost equal to the ionic rate of migration, in a solution as free from ions as could be obtained without unusual care. The spark discharge itself would, it is true, furnish an abundant supply of ions or ionic charges in the case of colloidal platinum, but the source of the negative charges on the quartz particles is not evident. The phenomenon of electrical endosmose, whereby water is usually carried to the cathode through porous walls of inert materials, as well as the fact that the quartz particles are nega-

tively charged, indicate that the particles are not simply inert bodies swept along by the ions resulting from the electrolysis. Besides, if the platinum and quartz are carried by hydroxyl ions, one would expect that the rate of migration would exceed that obtained for gold, where, especially in the first migration, the particles seem to be associated with chlorine ions. The effect of such impurities as carbonic acid must likewise be considered. The fact that the rate of migration of gold was the same for five successive migrations, however, whereby the chlorine must have been almost completely removed, indicates that the rate of migration of a boundary of colloidal gold would not be much changed if some other ion took the place of chlorine. That single gold particles migrate upward with the hydrogen ion in the "reverse movement" has already been pointed out. That they can be carried back and forth across the tube an indefinite number of times in the same experiment without a stable boundary, and that their primary direction of migration is quite independent of the acid or alkaline, oxidizing or reducing nature of the solution, will be shown farther on, thus indicating that the quartz and platinum are no more remarkable than the gold in their relations to ions.

It may be pointed out, further, that the magnitude of the gravity effect is apparently the same for gold, platinum and quartz, even though the density of the quartz is so much less than that of the metals. This probably arises from the fact that the largest suspensible particles of the different substances bear a constant inverse relation to their density. Thus the largest particles of quartz suspensible for a week or more are approximately 0.5 μ in diameter, whereas practically all of the microscopically visible particles of platinum settle out in a day or two. The growth of fungus in either case, building the colloidal particles into its mycelium,[1] renders it difficult to obtain precise information in this direction.

XI. FERRIC HYDROXIDE.

Ferric hydroxide precipitated from ferric chloride solution by an excess of ammonia at the boiling temperature, washed by decantation several times, then filtered and washed, was shaken up with a small amount of ferric chloride in solution. Disintegration gradually took place, with a continual lessening of the turbidity,

[1] *Cf.* p. 1341.

until, after some time, the liquid was scarcely turbid. The liquid was then dialyzed for more than a week against running tap water, then for several weeks against ordinary distilled water, frequently changed. When the dialysis was stopped the conductivity of the colloidal solution scarcely changed in twenty-four hours when dialyzed against fresh ordinary distilled water. Three months later this solution was diluted with two volumes of conductivity water, the resulting solution having a conductivity of 35.7×10^{-6}, and containing 1.850 grams ferric oxide per liter. Migrated downward (toward the cathode) with a potential difference of 220 volts in a tube 33.1 cm. long and 2.75 cm. in diameter, this solution gave the following results, the experiment being carried out in ordinary daylight.

TABLE XXXIII.

Colloidal "ferric hydrate."

First migration down. $\kappa_s = 35.7 \times 10^{-6}$; $\kappa_w = 75.1 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.167	2.0	12.0
2	0.42	4.0	8.0
3	0.62	5.6	8.0
4	0.95	8.1	7.5
5	1.67	14.5	8.9
6	2.33	20.2	8.5
7	3.67	30.2	7.5

Final κ water around anode (50 cc.) $= 1130 \times 10^{-6}$ (smelled strongly of chlorine).

Final κ water around cathode (50 cc.) $= 10.5 \times 10^{-6}$.

The rates given in the foregoing table closely resemble those obtained in other solutions where precipitation took place. In this experiment the formation of the precipitate could be watched, as the solution was transparent. The colloidal material was migrated clear to the bottom of the tube, where it became entirely insoluble in water, gelatinous and adhesive, still containing large amounts of chlorine. The density of the color of the colloidal solution remained constant during the migration. The large amount of conducting material eliminated around the anode (see table), together with the fact that the conductivity of the water in the tube was greatly increased during the migration (see κ_w in the table) show that the chlorine thus liberated had been in stable union with the colloid. In this connection it is interesting

to note that none of this chlorine is precipitated from the original solution by silver nitrate, even on boiling. Complete congelation gelatinizes the colloid and frees the chlorine (silver nitrate test). No lowering of the freezing-point could be detected.

Experiments made to determine the coagulative power of electrolytes when added to this solution confirmed the conclusion arrived at by Duclaux[1] that the polyvalent anions, as well as the hydroxyl ion, replace the chlorine in the compound $x\mathrm{Fe(OH)_3}.y\mathrm{FeCl_3}$. A nearly similar conclusion was arrived at by Hardy.[2]

XII. SILICIC ACID.

A very stable and pure solution of silicic acid may be obtained by dialyzing a water solution of solid water-glass (A), or the same solution to which a large excess of hydrochloric acid has been added (B). Either solution is finally acid to litmus and phenolphthaleïn, has a puckering taste, and is free from chlorine and sodium. The solutions, originally containing 100 grams of solid water-glass to the liter, contained (A) 5.63 grams, $\kappa = 67.6 \times 10^{-6}$, (B) 14.73 grams silica per liter, $\kappa = 100 \times 10^{-6}$. Neither solution gave any lowering of the freezing-point. Solution (B) was readily coagulated by a small amount of $m/300.\mathrm{AlCl_3}$, but neither solution was coagulated perceptibly by any other of the common electrolytes tested, except in strong or alkaline solution, or at the boiling temperature. Boiling alone was without effect. The following rates were obtained with solution (B) in a tube 37.85 cm. long and 1.2 cm. in diameter with a potential drop of 220 volts between straight platinum wire electrodes. The experiment was carried out in ordinary daylight.

TABLE XXXIV.

Colloidal silicic acid. First migration down and up. $\kappa_3 = 100 \times 10^{-6}$.

Distance from top. Centimeters.	Rate in centimeters per hour.	Distance from top. Centimeters.	Rate in centimeters per hour.
1.45	3.22	13.20	3.00
4.10	4.18	14.80	3.20
4.95	3.40	15.80	3.33
8.30	4.47	16.80	3.00
9.40	4.12	18.00	3.00
7.85	-5.5[1]	19.35	2.70

[1] Spontaneous double reversal.

[1] *Compt. Rend.*, **138**, 809 (1904).
[2] *Proc. Roy. Soc.*, **66**, 120 (1900).

TABLE XXXIV.—(*Continued.*)

Colloidal silicic acid. First migration down and up. $\kappa_s = 100 \times 10^{-6}$.

Distance from top. Centimeters.	Rate in centimeters per hour.	Distance from top. Centimeters.	Rate in centimeters per hour.
8.30	3.37	20.15	2.40
8.95	3.25	21.40	1.67
9.80	3.00	22.60	1.29
10.50	3.50	23.60	1.40
11.20	3.50	24.10	1.43
12.60	3.23	Change water at ends and reverse current.	
24.55	...	19.15	1.00
24.17	3.80	18.85	0.90
23.10	4.28	18.50	1.05
22.25	4.25	18.30	0.67
21.10	5.75	18.00	1.00
20.80	1.20	17.55	0.75
20.30	2.00	17.30	0.63
20.00	1.20	17.07	0.73
19.85	1.00	16.77	0.62
19.60	1.00	16.40	0.62
19.40	1.00	15.55	0.68

Final κ aq. top $= 16.9 \times 10^{-6}$; final κ aq. bottom $= 13.7 \times 10^{-6}$.

The rate of migration of silicic acid is seen to be distinctly less than that of the colloids previously worked with, the potential gradient in this experiment being substantially the same as that in the first series of experiments with gold, where the initial rate of migration was 1.90 cm. per hour for unit potential gradient, as against 0.55 cm. per hour in this experiment. The reverse effect was so great as temporarily to reverse the direction of migration of the boundary. The migrating boundary could be detected only by the difference in the index of refraction and in the second migration down finally stopped at a point one-tenth the distance from the bottom. The water above the boundary was then removed and the silicic acid found to be solid. This solid substance, insoluble in water and structureless when air-dried, lost 85.5 per cent. of water over calcium chloride within forty-eight hours, when its weight became constant for thirty hours. Ignited before the blast-lamp, this latter substance lost 16.1 per cent. of water, corresponding within the limits of error (the ignited silica was quite hygroscopic) to the formula $H_4Si_3O_8$.

	Calculated. Gram.	Found. Gram.
H_2O	0.0485	0.0470
SiO_2	0.2436	0.2451

XIII. THE REVERSE MOVEMENT IN THE MIGRATION OF COLLOIDS.

The "reverse effect" has been shown to be a general characteristic in the migration of colloids. The following experiments show further that this reverse effect is not due solely to the hydrogen ions migrating up the tube, but that part, at least, of the colloid itself is also moved in the direction opposite to that of the primary migration (see page 1358). It was found that the direction of migration, though not the rate, could be best studied in tubes placed horizontally, closed at both ends with goldbeaters' skin, with compartments at the ends containing the electrodes, past which conductivity water could be kept running. The electrodes and the tubes supplying the water entered the end compartments through rubber stoppers, as shown in the photographs. The water escaped through a hole cut in the upper side of the rubber band connecting the end tubes with the migration tube.

The colloidal solutions placed in the migration tube were as follows: A concentrated dialyzed and electrically purified red gold solution made in the manner previously described; a violet gold solution made by dialyzing against ordinary distilled water the red gold solution obtained by sparking gold electrodes in a 0.001-normal sodium hydroxide solution with a current of 10 to 12 amperes;[1] a concentrated red gold solution, prepared by digesting coagulated blue gold with ammonia (see page 1341); a greenish yellow silver solution prepared by sparking silver electrodes in conductivity water and dialyzing to remove the silver hydroxide with which the solution is contaminated.[2] The conductivities of these solutions varied from 5×10^{-6} to 80×10^{-6}. The results obtained with them were scarcely distinguishable, however, as will be shown. The migration tube was 24.2 cm. long and 2.75 cm. in diameter. The distance between the electrodes was 26.6 cm. The voltage was 220.

Under these conditions, with conductivity water running past the ends of the tube so fast that its conductivity is but slightly increased, usually from 2×10^{-6} to 4×10^{-6}, the following

[1] A more concentrated and more stable red gold solution may be obtained by sparking gold electrodes in the presence of a solution of hydrochloric acid having a conductivity of 200×10^{-6}.

[2] Blake: *Am. J. Sci.*, **16**, 431 (1903). The cathode lost 0.0507 gram, the anode 0.0698 gram. The conductivity increased from 3.3×10^{-6} to 17.5×10^{-6} during the sparking. A considerable amount of slime was deposited on the cathode from the undialyzed solution but not from the dialyzed solution under the given conditions.

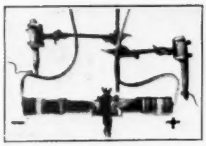

Fig. 2.
Bredig's gold solution, after one hour.

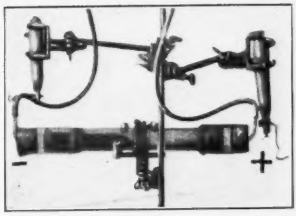

Fig. 3.
Ether-acetylene gold solution, after one hour.

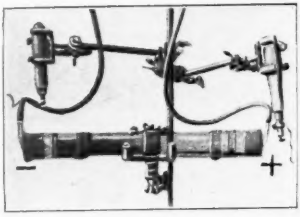

Fig. 4.
Same as Fig. 3, one hour later.

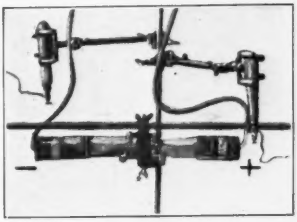

Fig. 5.
Bredig's silver solution, water at ends not running.

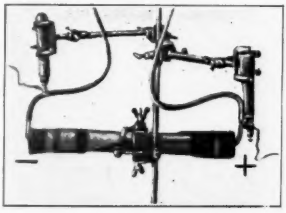

Fig. 6.
Same as Fig. 5, one-half hour later, water running.

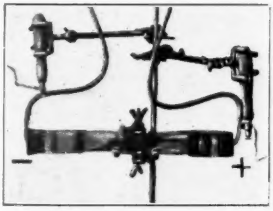

Fig. 7.
Same as Fig. 6, two hours later.

Fig. 8.
Gelatine, coagulated at *g*.

phenomena occur when contact is made. The colloid at once moves 1 or 2 mm. away from the cathode membrane with a sharp vertical surface of demarcation. This boundary then stops, the upper edge of it breaks and the colloid along the top of the tube moves rapidly toward the anode, leaving a streak of clear water behind. When this clear streak has nearly reached the anode membrane a V-shaped clearing occurs somewhere near the middle of the tube (Fig. 2), gradually extending downward and widening toward the anode (Fig. 3). Meanwhile a heavy solution of the colloid gathers on the bottom of the tube next to the anode membrane. This heavy solution soon begins to move back along the bottom of the tube toward the cathode, whether the current is kept running or is turned off, evidently due to gravity in the latter case. When the current is kept running, the heavy solution soon accumulates against the cathode membrane. The colloid still remaining in dilute solution in the upper portion of the cathode end of the tube, as well as the heavy solution accumulated against the cathode membrane and extending as a thin layer on the bottom of the tube throughout its entire length, now assume an unending variety of formations, some of the more characteristic of which are shown in the photographs (Figs. 4 to 7). The conditions governing these motions have not been fully ascertained. Although further work in this direction is contemplated, a preliminary statement may be made here. If the current is allowed to run for several hours without changing the water at the ends of the tube, then the colloid may be made to migrate from either pole by allowing pure water to flow slowly through the compartment surrounding the pole from which the repulsion takes place; after several hours the colloid is sometimes again attracted to the pole at which the pure water is flowing. On one occasion a deposit of soluble mud (red gold) which had formed on the anode membrane was removed by the action of the current.

An experiment made with the same silver solution in the same sort of vertical tube used for the migration experiments shows further the complexity and sensitiveness of the reverse movement and indicates another cause for the instability of the migrating surface with gold and other colloids in the upper portions of the tube. It was found that when the silver solution was contained in a tube 48.5 cm. long and 2.45 cm. in diameter and a potential

difference of 220 volts was applied with the cathode at the top, in the dark, the colloid moved 1 or 2 cm. away from the upper membrane in the first ten minutes and then moved back again the next ten minutes. When fresh water was added at the top, this process was repeated many times. It thus appears that the initial rate of migration of colloidal silver, independent of the "reverse movement," is about the same as that of gold.

XIV. EXPERIMENTAL CRITICISM OF BILLITZER'S HYPOTHESES.

It will be evident at once that the results thus far recorded are very different from what would be expected from a consideration of the hypotheses propounded by Billitzer in the work cited in §II. In this connection it will be convenient to distinguish the "reverse movement," above described, from a change in the direction of the primary migration, which we shall speak of as a "reversal." A direct attempt to repeat the work of Billitzer on the change in the direction of migration of colloids due to the presence of various electrolytes, failed to reveal any reversals with Bredig's platinum or with red colloidal gold solutions like those used in the migration experiments, whether the colloid was uncontaminated, or mixed with urea as in Billitzer's experiments. The experiments were tried with the apparatus used by Billitzer—a U-tube—and with vertical tubes like those heretofore described. The amount of electrolyte added to the solution to reverse the direction of migration was varied from a trace to amounts so large that the migrating surface was broken up by the heating effects of the current. The voltage was 110 or 220.

Billitzer added gelatine also to his solutions to prevent the coagulation of the metallic colloid by the electrolytes added, according to principles now well recognized.[1] The effect of adding 0.5 gram per liter of the purest commercial gelatine to the platinum solution whose rate of migration has already been given, is shown in the following table of rates similarly obtained. The tube was 48.5 cm. long and 2.45 cm. in diameter, with 100 cm^3. of conductivity water at the top and 150 cm^3. at the bottom. The voltage was 220, with the anode at the top. Strong light was excluded.

[1] We are informed by private correspondence that the amount of gelatine added was variable and "recht viel," especially with the platinum solutions.

TABLE XXXV.

Bredig's platinum hydrosol + 0.5 gram gelatine per liter.

$\kappa_{18} = 31.8 \times 10^{-6}$.

Anode at the top.

No.	Time in hours.	Distance from top in centimeters.	Rate in centimeters per hour.	Surface No.
1	1.17	0.05	0.43	1 Clear above this surface.
2	3.17	0.0	....	
3	3.17	42.1	(2.0)	
4	3.37	41.2	4.5	
5	4.12	40.3	1.2	2 Darker below the surface.
6	4.53	Indistinct, settling.		
7	4.53	0.8	....	
8	22.53	5.9	0.33	
9	24.53	6.4	0.25	
10	30.03	9.4	0.75	3 Same as Surface No. 1.
11	51.03	15.2	0.28	
12	53.03	15.8	0.30	
13	69.03	18.9	0.19	
14	70.0	Rising	....	
15	75.42	16.0	....	

The history represented by the foregoing rates is easily told. At first, part of the material was carried to the lower membrane without a surface of demarcation. At reading No. 3 this material had already migrated 6.4 cm. up the tube (42.1 cm. from the top).[1] Meanwhile all the material had slowly migrated 0.5 cm. downward from the top and then migrated back to its original position (reading Nos. 1 and 2). Surface No. 2 then continued to migrate upward for an hour or so (reading Nos. 4 to 6). It then reversed and simultaneously a new surface—No. 3—formed at the top. This surface slowly migrated downward for a couple of days, and then began to rise. The rate going up is much greater than the rate going down. When the cathode was at the top, the results were equally unsatisfactory, the first migration being towards the cathode.

One might surmise that such an effect as that just described was due to mixed influences, evidently introduced by the gelatine added. An idea as to what these influences are may be gathered from the migration of gelatine alone, similarly placed, except that the cathode was at the top and the solution contained 2 grams of gelatine per liter.

[1] *Cf.* Lehmann's experiment, p. 1343.

TABLE XXXVI.

Migration of gelatine. Cathode at the top. $\kappa_S = 68 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.	
1	1.17	4.5	3.9	Read by index-of-refraction surface.
2	1.58	6.2	4.1	
3	1.92	6.2	0.0	Current off.
4	2.58	6.2	0.0	
5	3.08	7.9	3.4	
6	4.58	9.1	2.4	
7	19.17	14.5	0.35	Top of gelatine coagulated.
8	21.67	15.2	0.28	
9	25.67	15.9	0.17	
10	42.0	Coagulated down to 23.5, ragged.		
11	216.0	No further change—photograph.		

The index-of-refraction surface used at first as the surface of demarcation of the gelatine was especially sharp, like that of silicic acid. All the gelatine was finally collected in the middle of the tube, as shown in the photograph (Fig. 8), where it coagulated and adhered to the glass. Hence the gelatine migrated away from both poles. That the downward migration was not due to gravity is shown by the result obtained by breaking the current, when the gelatine, not yet coagulated, remained unchanged (reading Nos. 3 and 4).

The gelatine solution was originally acid to phenolphthalein and the electrolytes eliminated around the anode contained sulphuric acid. Since the original gelatine solution was acid, the gelatine should, in agreement with the results obtained by Hardy with egg albumen and globulin, have been repelled more strongly from the anode than from the cathode. This was the case, even though the cathode repulsion was aided by gravity. In fact, when the poles were reversed (separate experiment) all the gelatine was finally found on the bottom of the tube in the coagulated state.

These facts show that it would be practically impossible to trace the movements of colloidal platinum in the presence of gelatine and as distinguished from the gelatine, owing to mutual influences. It should be remembered that in the experiment recorded in Table XXXV the two substances were present in nearly the same proportion, since Bredig's platinum hydrosol usually contains about 0.2 gram platinum per liter, and that the

platinum alone migrates to the anode and the gelatine the more actively to the cathode. This conflict, continually modified by the action of the electrolytically freed acid and alkali on the gelatine, and by the coagulation of the gelatine, resulted in several reversals of the direction of migration, as is shown in the table. That one colloid will not diffuse through another was discovered by Graham. That suspended particles are carried down by the precipitation of gelatine and gums has been known for a long time. Hence it was scarcely to have been expected that platinum would migrate through gelatine uninfluenced by it. Billitzer found, in fact that his "platinum" (gelatine and platinum) moved to the cathode when considerable amounts of the (acid) electrolytes were present, as we have seen the gelatine alone would do. Hence the platinum was evidently carried along by the gelatine. With less of the acid electrolytes present Billitzer found that the "platinum" moved to the anode. Since in the presence of less acid the gelatine would tend less strongly to migrate toward the cathode, it is probable that in this case the platinum, tending to migrate to the anode, carried the gelatine along with it to some extent. The fact that the direction of migration is often opposite in the two arms of the U-tube makes it difficult to interpret Billitzer's results, but it would seem that most of his "reversals" obtained with "platinum" may be thus accounted for.

In attempting to repeat Billitzer's experiments with colloidal silver a true reversal, or primary migration from the anode, was obtained without the addition of gelatine. Silver nitrate or nitric acid was added to the undialyzed colloidal silver solution until the normality was about 0.008 or 0.004, respectively. When either of these solutions was placed in one of the vertical tubes used for the migration experiments with gold under exactly similar conditions, in the dark, with 50 cm^3. of water at each end, with the anode at the top, the colloid migrated down about .1 cm. in the first half hour and then remained stationary for twenty-four hours. The same thing was obtained when urea was added, and a primary migration from the anode was also obtained in a U-tube under the conditions prescribed by Billitzer, except that no gelatine was added to the solution. The conductivity of these solutions was about 1000×10^{-6}; it was somewhat less, however, when urea was present. It may be added that urea alone tends to prevent the coagulation of metallic colloids either by electrolytes or by the electric current.

XV. THEORETICAL DISCUSSION.

The theoretical aspect of the experimental results of this investigation may be entirely included under the relation of colloids to electrolytes. The most probable explanation of the observed phenomena is that the migration of colloids by the electric current is due to the association of the colloidal particles with ions. From this point of view it is very remarkable that the rate of migration of the colloidal particles[1] and associated ions should be of the same order of magnitude as that of free ions.

An idea as to the nature of the union between the ions and the colloidal particles may be best obtained from the experiments relating to the "reverse movement" of the colloid when migrated in horizontal tubes. It was shown for gold prepared by three different methods, and for silver prepared by Bredig's method, that the colloid could be repelled from both poles simultaneously or repeatedly swept back and forth across the tube from one pole to the other by varying the strength of the acid accumulated at the anode and of the base accumulated at the cathode by the action of the current. The concentration of acid or base necessary to produce this effect was only that accumulated from ordinary or conductivity water and the enclosing vessels by the action of the current for a few minutes under the given conditions. In fact, no lower limit was found for the conductivity of the water at the one end of the tube necessary to produce the foregoing effects, provided that of the water at the other end was still less. This behavior may be due to the fact that the colloidal particles are swept along by the hydrogen ions coming from the anode and by the hydroxyl ions coming from the cathode, with the formation of a cloud of neutral particles at the point where the two influences meet (see Figs. 5, 6 and 7). The fact, often noted, and clearly shown in Fig. 5, that this neutral cloud forms at a point very nearly three-eighths of the distance from the cathode to the anode when the tube is undisturbed, confirms this belief, since this is the ratio of the rate of migration of the hydroxyl to the hydrogn ion. The greater mobility of the hydrogen and hydroxyl ions compared to any other ions they may be associated with to maintain the electrical neutrality of all parts of the solution may be

[1] On the size of colloidal particles, see Lobry de Bruyn: *Rec. trav. chim. Pays-Bas*, **19**, 251 (1900); Siedentopf and Zsigmondy: Drude's *Annalen*, **4**, 1 (1903); Ehrenhaft: *Ibid.*, **11**, 489 (1903).

assigned, as was done by Hardy,[1] as a sufficient reason why the colloidal particles would be swept along by the hydrogen and hydroxyl ions, after the primary migration is over, and not swept in the opposite direction by the other ions just mentioned. The fact that Billitzer's hypotheses bearing on this subject could not be confirmed indicates that the colloidal particles are not ion-electrodes in equilibrium with the solution surrounding them, and the results obtained regarding the gradual purification of colloidal gold solutions, first by dialysis of free electrolytes, then by electrolysis of associated electrolytes, renders it highly probable that the union in question is similar to that occurring in so-called "adsorption" phenomena. It would seem, in fact, that the union is quite stable and that the sign of the electric charge is generally reversed only at the electrodes. This tendency of the ions to attach themselves to colloidal particles in water may be identical with that noted in gases by J. J. Thomson and others.

Until more is known about the great resistance encountered by the ions during electrolysis it would be idle to speculate as to why the presence of an associated colloidal particle does not increase that resistance, even though the colloidal particle is surrounded by a water envelope.[2] In this connection it is interesting to note that Smoluchowski,[3] applying the theory of the electrical double layer devised by Helmholtz to explain the phenomenon of electrical endosmose, and using as the potential between the layers of the double sheet the value calculated by Helmholtz from Wiedemann's observations on electrical endosmose, has deduced the conclusion that the rate of migration of particles suspended in water should be of the same order of magnitude as that of the ions. That the rate should be independent of the size and shape of the particles was previously deduced by Lamb.[4] We find, therefore, a theoretical explanation of the otherwise remarkable fact that the association of colloidal particles with ions does not greatly retard their rate of migration, a fact which seems to indicate that the electrical double sheet existing around a single charged particle may be only that due to a single ion associated with it. It is only necessary to add, in view of the experimental confirmation which these theories have received in the foregoing

[1] *Jour. physiol.*, **29**, cit.

[2] See Parks : *Phil. Mag.*, **4**, 240 (1902) ; **5**, 517 (1903) for literature to date.

[3] *Bull. Acad. Sci. de Cracovie*, March, 1903, p. 182 ; *Ref. Phys. Chem. Rev.*, I, p. 124.

[4] Brit. Assn. Report, 1887, p. 502.

pages, that the electrical moment of the double sheet would seem to offer a sufficient explanation of the permanent suspensibility of particles whose density is greater than that of the suspending medium and to place them in the same state as that of heavy ions so far as suspensibility is concerned.

That the density of the suspended particles is greater than that of water is shown in a number of ways. Thus Cholodnyj[1] showed that the density of silver in colloidal solution is equal to that of the metal in the massive state. A density of the gold particles greater than one would be necessary to account for the falling of gold solutions into pure water, as noted on page 1365. A marked gravity effect was obtained in the vertical migrations by noting the difference in the rate up and down, and in the horizontal migrations by noting the actual settling of the colloid to the bottom of the tube. So, also, when quartz particles, which retained the optical properties of massive quartz, were precipitated by the addition of an electrolyte, no aggregation could be detected under the microscope, showing that the settling was not due to a condensation of the colloidal substance.

Not only the migration and the permanent suspensibility of colloidal particles may be thus attributed to the presence of ions, the diffusion observed with colloidal gold may likewise be due to the diffusion of the ions associated with it. However that may be, it is plain that the fact that the gold does diffuse offers a probable explanation of the Brownian movement in this case.

Another interesting phenomenon is also shown most clearly in the diffusion experiments, that is, the stability of the boundary or surface of demarcation.[2] According to the law applicable to the gold solution as a whole, that is, that the rate of diffusion varies as the concentration of the gold in solution, the concentration of the gold solution at any moment should be greatest at the bottom, gradually falling to zero at the top. We have seen that a dense boundary forms, however, as though the gold might migrate faster in the gold solution than into pure water. The stability of the boundary is strikingly shown, also, in the migration experiments made in vertical tubes, in which the boundary usually remains unbroken to the end of the experiment, even though subjected to the many influences revealed by the migrations made in

[1] *J. Russ. Phys. Chem. Soc.*, **35** (2), p. 585 (1903); *Ref. Phys. Chem. Rev.*, I, p. 125; *Chem. Centrbl.*, 1904, I, p. 634.

[2] *Cf.* Barus: Bull. 36, U. S. Geol. Survey.

horizontal tubes. It is plain that the rate of migration of the boundary obtained in the vertical tubes is, on account of the component forces acting in it, only a minimum value for the rate of migration of the single untrammeled particles.

It may be remarked in conclusion that the relation between colloidal particles and ions pointed out in this work may be expected to throw some light on the principles involved in the coagulation of colloids by electrolytes.

SUMMARY.

It has been shown by this investigation that:

(1) Colloidal gold solutions, prepared by the action of an ethereal solution of gold chloride on an aqueous solution of acetylene, retain, even after prolonged dialysis against conductivity water, a constant conductivity five or six times as great as that of the water outside the dialyzer.

(2) This conductivity is almost completely lost by repeatedly migrating the gold downwards with the electric current against a membrane of goldbeaters' skin and redissolving it in pure water, and is to that extent, at least, attributable to electrolytes associated with or "adsorbed" by the gold.

(3) Red gold was obtained as a soluble mud by migrating it against a membrane of goldbeaters' skin; from this, mud solutions of any desired concentration and of great purity were prepared.

(4) Colloids may readily be made to migrate downward with a sharp boundary or surface of demarcation when the colloidal solution is placed in a vertical tube.

(5) This boundary is not readily disturbed by slight temperature changes; neither is it disturbed by the action of light unless the colloidal material is opaque.

(6) The rate of migration of this boundary, under optimum conditions, was determined for gold, platinum, silver, Prussian blue, "ferric hydrate," silicic acid and gelatine.

(7) The rate of migration of colloids is determined primarily by the potential gradient and is directly proportional to it.

(8) The boundary is stable when the potential gradient just above the boundary is greater than that just below it.

(9) The potential gradient, and hence the rate of migration in the different sections of the tube, may be calculated approximately from a knowledge of the initial conductivity of the colloidal solution and of the water above the migrating surface.

(10) An influence due to the force of gravity becomes manifest during the migration.

(11) Gold solutions fall rapidly through pure water without mixing with it.

(12) The soluble mud obtained by downward migration, when placed under pure water, diffused upward into it at a rate comparable with that of electrolytes diffusing from concentrated solutions into pure water.

(13) A reverse effect, consisting either in a sudden retardation of the downward movement of the boundary or in a reversal of its direction, occurs in the migration of colloidal solutions in vertical tubes. This is due, in part, to changes in the potential gradient arising from the decomposition products of electrolysis, and in part to a reverse movement of the colloid itself where precipitation by the current is not complete.

(14) The reverse movement of colloids can best be studied by migrations carried out in horizontal tubes closed at the ends with goldbeaters' skin past which conductivity water may be kept flowing.

(15) The reverse movement was thus shown to be complex, the colloid being carried repeatedly back and forth between the poles as though swept along by the hydrogen and hydroxyl ions after the primary migration had taken place.

(16) A change in the direction of the primary migration was obtained with colloidal silver, but not with gold or platinum, by adding certain electrolytes to the solution.

(17) Gelatine migrates simultaneously from both electrodes.

(18) When a mixture of gelatine and platinum in colloidal solution is migrated, each colloid exerts an influence on the migration of the other.

(19) The "reversals" obtained by Billitzer were probably due to the effect of the migration of the gelatine, superimposed on that of the metallic colloids present with it.

(20) The rate of migration of the boundary, independent of gravity, diffusion and the reverse effect, in the case of colloidal gold, platinum, silver, Prussian blue, "ferric hydrate" and quartz, is approximately that of the univalent ions of neutral inorganic salts.

(21) These facts are in agreement with the deductions of Lamb and Smoluchowski, based on the theory of the electrical double

layer, according to which the rate of migration of solid particles suspended in water should be independent of the size and shape of the particles, and should be of the same order of magnitude as the rate of migration of the ions.

(22) The charge on the colloidal particles is probably due to associated ions, which determine the migration, diffusion and permanent suspensibility of the particles.

This investigation will be continued during the following year.

NOTE.

A Contact Process for the Preparation of Ammonia-free Water.—The preparation of ammonia-free water in chemical and water laboratories has usually been limited to one or two tedious processes. Although otherwise inexpensive, the time required and the necessary strict attention to sources of ammonia from corks and joints, as well as the continual testing of the product, have made this chemical a decided luxury. Difficulty in getting certain rather poor waters absolutely satisfactory by the usual distillation induced the author to try the contact process which is described in this article.

A standard method for the preparation of ammonia-free water is tersely described in Richards and Woodman's "Water, Food and Air," as follows: "The ammonia-free water used in this laboratory is made by redistilling distilled water from a solution of alkaline permanganate in a steam-heated copper still..... only the middle portion of the distillate is collected." Modifications of this method are the only procedures described in the literature on water analysis for ammonia-free water, one exception being the method of Weems, Gray and Myers,[1] *using* sodium peroxide.

It is sufficient to say that either process is inefficient and troublesome, even if the final product is satisfactory, which, indeed, is not always the case.

I will now describe a process by which waters containing any ordinary amount of carbonaceous or nitrogenous material can be rendered perfectly free from the same, and the whole done by a process extremely simple in outline.

[1] *Proc. Iowa Acad. Sciences*, **10**, 112, and abstract *J. Soc. Chem. Ind.*, **22**, 1016.

The method is based on the catalytic powers of finely divided platinum, hence it may be called a catalytic contact process. The steam from the water-boiler is made to pass through a mass of platinized asbestos which is heated to redness. On contact with this reagent any organic or nitrogenous material, or even ammonia itself, is completely broken up and the distillate collected will be found perfectly ammonia-free. Other contact substances are more or less sufficient, but usually require the presence of air, which is not necessary with platinum.

This process requires one distillation only and no chemical whatever; every bit of the distillate is satisfactory, if the contact was at the right temperature before starting the steam through. The apparatus required is, of course, quite simple. The precautions to be observed are chiefly the following:

The contact substance must be porous so as to offer no hindrance to the passage of the steam.

The contact should be held firmly so that sudden puffs of steam do not dislodge and pack the material.

The contact material ought to be heated to redness and kept at this temperature during the distillation.

The distillate will be very hot and the tin condenser used should be thoroughly cooled where it joins the contact tube. Of course, the water will collect in the front end of the contact tube unless it is kept hot, also, if a glass tube is used and any packing of the contact occurs, the tube yields to the pressure and soon bursts. To obviate cracking and bursting, metal tubes should be used. The tube can be joined directly to the condenser tube by soldering, while a litharge-glycerine joint will serve admirably at the boiling-end.

By properly observing these precautions the process works successfully and from the poorest water will furnish quickly and easily a most satisfactory product. H. B. PULSIFER.

NEW HAMPSHIRE COLLEGE,
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